Detection of interstellar CH\textsubscript{3} \textsuperscript{1}

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ABSTRACT

Observations with the Short Wavelength Spectrometer (SWS) onboard the Infrared Space Observatory (ISO) have led to the first detection of the methyl radical CH$_3$ in the interstellar medium. The $\nu_2$ $Q$–branch at 16.5 $\mu$m and the $R(0)$ line at 16.0 $\mu$m have been unambiguously detected toward the Galactic center SgrA*. The analysis of the measured bands gives a column density of $(8.0 \pm 2.4) \times 10^{14}$ cm$^{-2}$ and an excitation temperature of $(17 \pm 2)$ K. Gaseous CO at a similarly low excitation temperature and C$_2$H$_2$ are detected for the same line of sight. Using constraints on the H$_2$ column density obtained from C$^{18}$O and visual extinction, the inferred CH$_3$ abundance is $(1.3^{+2.2}_{-0.7}) \times 10^{-8}$. The chemically related CH$_4$ molecule is not detected, but the pure rotational lines of CH are seen with the Long Wavelength Spectrometer (LWS). The absolute abundances and the CH$_3$/CH$_4$ and CH$_3$/CH ratios are inconsistent with published pure gas-phase models of dense clouds. The data require a mix of diffuse and translucent clouds with different densities and extinctions, and/or the development of translucent models in which gas-grain chemistry, freeze-out and reactions of H with polycyclic aromatic hydrocarbons and solid aliphatic material are included.

Subject headings: Line: identification — ISM: abundances — ISM: lines and bands — ISM: molecules — Galaxy: center — Infrared: ISM: lines and bands
1. Introduction

The methyl radical CH$_3$ is an important intermediate product in the basic ion-molecule gas-phase chemistry networks in the interstellar medium driven by cosmic-ray ionization (Herbst & Klemperer 1973). Together with CH and CH$_2$, it is produced by a series of reactions starting with C + H$_3^+$ → CH$^+$ + H or the radiative association of C$^+$ + H$_2$ → CH$_2^+$ + h$\nu$, followed by hydrogen abstraction reactions and dissociative recombination. Alternatively, it can be produced by photodissociation of methane (CH$_4$). Subsequent reactions of C$^+$ with CH$_3$ form one of the most important steps in the formation of more complex hydrocarbons.

The ion H$_3^+$ which initiates the chemistry in the cold gas has been detected only recently toward the Galactic center by Geballe et al. (1999) at a surprisingly high abundance. This unique line of sight turns out to be an extremely valuable environment to study abundances in the cold low density interstellar medium, since even minor species like CH$_3$ may be detectable due to its long path.

Although CH$_3$ is a simple species, it is difficult to obtain accurate laboratory measurements of its molecular parameters since, as a radical, it recombines very fast with other particles in a gas. Herzberg (1961) and Herzberg & Shoosmith (1956) were the first to determine that the molecule is planar, but definite proof came only from measurements of the out-of-plane bending mode $\nu_2$ at 16 $\mu$m by Yamada et al. (1981).

Observations of the 16–16.5 $\mu$m wavelength range are strongly hampered from the ground due to the Earth’s atmosphere. The first detections of CH$_3$ in space have become possible only using the Infrared Space Observatory (ISO) (Kessler et al. 1996). Bézard et al. (1998, 1999) have recently detected CH$_3$ in the atmospheres of Saturn and Neptune respectively, but no previous searches for the molecule in interstellar space have been reported.
2. CH₃ spectroscopy

Since the CH₃ radical is planar and symmetric, it does not have electric dipole allowed rotational lines which could be detected in the (sub-)millimeter wavelength range. The planar nature also implies that the symmetric stretch $\nu_1$ is infrared inactive and the asymmetric stretch $\nu_3$ at 3.16 $\mu$m relatively weak. Indeed, the transition dipole moment of the $\nu_3$ band is found to be a factor of three weaker than the out-of-plane bending mode $\nu_2$ (Triggs et al. 1992, Amano et al. 1992).

To calculate the $\nu_2$ spectrum, the term energies were taken from Yamada et al. (1981). The nuclear spin of the H-atoms can couple either to a quartet or doublet state, with nuclear spin statistical weights of 4 and 2, respectively. Because CH₃ follows Fermi-Dirac statistics, the $K = 3, 6, 9, \ldots$ levels are quartet states, and the other $K$-values doublet states. The strongest $Q$-branch has $N = K$ and is located at 16.5 $\mu$m; the strongest other feature is the $QR(0)$ line at 16.0 $\mu$m thanks to its favorable Hönl-London factor. The band strength of $(2.5 \pm 0.8) \times 10^{-17}$ cm$^{-1}$ (molecule cm$^{-2}$)$^{-1}$ was taken from Wormhoudt & McCurdy (1989). The calculation of the spectrum was performed as described in Helmich (1996).

The shape of the spectrum is very sensitive to the excitation temperature (see Figure 7.14 of Helmich 1996). Besides the strong $QQ$-branch and $QR(0)$ lines, many more features become visible at excitation temperatures above 25 K, most notable the satellite $RQ$-branch at 16.53 $\mu$m and the $P(2)$ line at 17.60 $\mu$m.

3. Observations and Data Reduction

Observations were carried out in the SWS grating mode AOT06 (de Graauw et al. 1996) at a spectral resolving power $R = \lambda/\Delta\lambda \approx 1500 - 2200$. The spectral range covering the CH₃ $Q$-branch and the $P(2)$ line has been measured on 1997 February 21 15:24:27-19:03:01
UT, whereas that covering the \( R(0) \) and \( R(1) \) lines has been obtained on the same day at 19:03:45-20:55:41 UT. The SWS aperture size was 14" × 27" and has been centered on the position of Sgr A* RA 17\(^{h}\)45\(^{m}\)40\(^{s}\).0, Dec −29°00'28".6 (J2000 coordinates), with the long side of the slit oriented within 1 degree of the north-south direction. Due to the rather large aperture size, the Galactic center sources IRS 1, 2, 3 and 7 also fall inside the beam (see, e.g., Geballe et al. 1989), whereas IRS 5 and 6 are positioned just outside the slit.

Data were processed within the SWS interactive analysis system, based on the standard ISO pipeline OLP V8.7 products. The data reduction adhered to the recommendations of Salama et al. (1997). Raw data were rebinned to \( R = 5000 \), a value significantly larger than the actual spectral resolving power of the SWS to avoid losing spectral detail when convolving the observed data samples by the bin.

The absolute calibration of the SWS data has about ±20% uncertainty on average longwards of ∼15 \( \mu m \) (Salama et al. 1997). However, since our analysis is entirely based on spectra where the continuum is divided out, the actual uncertainty in the results is determined by the noise in the data rather than the actual calibration uncertainty. The main limitation of our analysis originates from the ±30% uncertainty in the CH\(_3\) \( \nu_2 \) band strength (Wormhoudt & McCurdy 1989, Yamada & Hirota 1983).

4. CH\(_3\) results

As shown in Fig. 1, the \( Q \)-branch at 16.5 \( \mu m \) and the \( R(0) \) line at 16.0 \( \mu m \) are clearly detected. This represents the first unambiguous detection of CH\(_3\) in the interstellar medium. The upper limit on the \( P(2) \) line at 17.60 \( \mu m \) provides an important constraint on the temperature. Due to a blend with the [Ne III] 15.555 \( \mu m \) atomic fine structure line at the SWS grating resolution, no information from the \( R(1) \) line at 15.54 \( \mu m \) could be obtained.
Both the $Q$-branch and the $R(0)$ lines are shifted with respect to their expected LSR wavelengths by about $-20$ km s$^{-1}$. Although such a shift is close to the SWS wavelength calibration accuracy (Valentijn et al. 1996), a $V_{\text{LSR}} = -30$ km s$^{-1}$ component of cold molecular gas has been reported previously by several authors from observations at radio and millimeter wavelengths with similar beam sizes (Serabyn et al. 1986 and Sutton et al. 1990, CO; Pauls et al. 1996, H$_2$CO; Serabyn & Güsten 1986, NH$_3$; Marr et al. 1992, HCO$^+$; Güsten et al. 1987, HCN; Bolton et al. 1964, OH). In all cases several velocity components at $\sim -50$, $-30$ and $0$ km s$^{-1}$ have been observed at much higher spectral resolutions. The relative strengths of these three components vary between the observed species with the $0$ km s$^{-1}$ component often the largest. At the SWS spectral resolution of $\sim 150$ km s$^{-1}$ it is not possible to distinguish between these different velocity components, but our observed shift is consistent with a mix of them. The location of the absorbing gas can therefore not be attributed to one particular feature, but is possibly spread along the line of sight toward Sgr A$^*$ among spiral arms and molecular clouds.

Fits of synthetic spectra to the data, as described in §2 and matching the SWS resolution, were performed for different excitation temperatures (10 to 50 K), different Doppler parameters ($b$ between 1.5 and 30 km s$^{-1}$) and column densities. The best fit to the individual absorption depths (Fig. 1 a,b) as well as their ratio (Fig. 1 c) is given in Table 1. The absorption depths are almost independent of Doppler parameter, and are mainly a function of column density. The ratio of the depths is a strong function of the excitation temperature. The inferred low excitation temperature of $(17 \pm 2)$ K from the $16.0/16.5$ $\mu$m ratio of $(0.8 \pm 0.15)$ is consistent with the non-detection of the P(2) line. Because CH$_3$ has no dipole moment, the populations of the lowest rotational levels are controlled by collisions, so that the excitation temperature is close to the kinetic temperature.

The H$_2$ column density along the line of sight has been constrained by several sets
of observations. First, the measured extinction of 31 mag (Rieke et al. 1989) implies $N(H_2) \approx 2 \times 10^{22} \text{ cm}^{-2}$ using $N_H/A_V = 1.9 \times 10^{21} \text{ cm}^{-2} \text{ mag}^{-1}$ and assuming that at least half of the hydrogen is in molecular form. Second, the detection of at least one optically thin C$^{18}$O line (R(0) at 4.7716 $\mu$m) in our ISO-SWS observation together with the measured CO excitation temperature of 8-13 K implies $N(C^{18}$O$) = (2 \pm 0.5) \times 10^{16} \text{ cm}^{-2}$. This is in good agreement with the analysis by Moneti & Cernicharo (2000) on the same data. Using $^{16}$O/$^{18}$O = 300 (Wilson & Rood 1994) and CO/H$_2$=$10^{-4}$ implies $N(H_2) \approx 6 \times 10^{22} \text{ cm}^{-2}$. We adopt $N(H_2) = (6 \pm 3) \times 10^{22} \text{ cm}^{-2}$, leading to a CH$_3$ abundance with respect to H$_2$ of $x$(CH$_3$) = $(1.3^{+2.2}_{-0.7}) \times 10^{-8}$. Note that all abundances would be increased by a factor of 3 if the lower H$_2$ column density derived from the extinction is used.

5. Related species: CH$_4$, C$_2$H$_2$ and CH

The availability of the full SWS scan allows searches for other chemically related molecules. Specifically, the $\nu_2/\nu_4$ dyad of CH$_4$ occurs around 7.7 $\mu$m and has been observed with the ISO-SWS toward massive protostars by Boogert et al. (1998). Toward the Galactic center, however, gas-phase CH$_4$ is not detected. Adopting the same excitation temperature as found for CH$_3$, an upper limit for its abundance of $\leq 1 \times 10^{15}$ cm$^{-2}$ is found. Solid CH$_4$ is clearly detected by Chiar et al. (2000) toward Sgr A* with a column density of $(3.0 \pm 0.7) \times 10^{16}$ cm$^{-2}$. Thus, most of the CH$_4$ is in solid form, consistent with the low temperature.

Detection of a blend of the pure rotational lines of CH at 149.09 and 149.39 $\mu$m towards the Galactic center has been reported by White et al. (1999). We have re-analyzed the LWS observations carried out on 1998 February 20 10:11:34-11:06:44 in the LWS01 grating mode (Clegg et al. 1996) at a resolution of $\sim 1500$ km s$^{-1}$ (Fig. 2 a). The LWS data reduction has been based on OLP V8.7 products and has been carried out within ISAP (Sturm et al.
1997). Outliers have been removed by iterative sigma clipping and the different scans have been flatfielded to their mean value by applying a second order polynomial offset to each individual scan. The fringing in the LWS data, present in all extended source observations has been removed by the dedicated module within ISAP. The inferred equivalent width for the unresolved doublet is $(85 \pm 5)$ km s$^{-1}$. Using the formulae from Stacey et al. (1987) and assuming $T_{\text{ex}}=17$ K, this leads to $N(\text{CH}) \approx (1.1 \pm 0.1) \times 10^{15}$ cm$^{-2}$.

Finally, the $\nu_5$ band of gas-phase $\text{C}_2\text{H}_2$ at 13.7 $\mu$m is clearly detected (Fig. 2 b). Following the analysis of Lahuis & van Dishoeck (2000), we find $N(\text{C}_2\text{H}_2) = (5.5 \pm 0.8) \times 10^{14}$ cm$^{-2}$ assuming $T_{\text{ex}} = 17$ K. Table 1 summarizes the results obtained from ISO observations. Note that the relative abundances of the molecules have much smaller error bars than the absolute values since the uncertainty in the $\text{H}_2$ column density cancels out.

### 6. Chemistry

The absolute and relative abundances of the observed molecules have been compared with a wide variety of models, including time- and depth-dependent models. None of the published pure gas-phase dense cloud models can reproduce the observations of all species (e.g., Millar et al. 1997, Lee et al. 1996, see Table 2). In general, the model CH$_3$ abundances are too low and the CH$_4$ abundances too high. Also, the model abundance of C$_2$H$_2$ is significantly smaller than that of CH$_4$, in contrast with observations. The only models which come close to matching the absolute and relative abundances of CH$_3$ and CH$_3$/CH and CH$_3$/CH$_4$ are low-density translucent cloud models with $n(\text{H}_2) \approx 10^3$ cm$^{-3}$ and $A_V \approx$ few mag, so that photodissociation of CH$_4$ to CH$_3$ and CH$_2$ is still efficient. Table 2 lists recent model calculations by Terzieva & Herbst (priv. communication) and results based on the models by van Dishoeck & Black (1986) and Jansen et al. (1995) using updated branching ratios for the dissociative recombination of the hydrocarbon ions (Andersen et al. 2000).
Low metal abundances are favored, to prevent destruction of the hydrocarbons by oxygen and by sulfur atoms and ions. Note, however, that even though the abundances at $A_V \approx 3$ may match the data within a factor of a few, the CH$_3$ column density in such models is only $1 \times 10^{13}$ cm$^{-2}$, nearly two orders of magnitude below observations. At the same time, the CH column density of $1.4 \times 10^{14}$ cm$^{-2}$ is a factor of 10 below observations. Because of the strong depth dependence of the CH, CH$_3$ and CH$_4$ abundances, it is not possible to reproduce the column density ratios with these same models. The large observed H$_3^+$ column density suggests that there are several clouds along the line of sight. Some combination of low-density diffuse clouds to produce the CH and denser clouds to account for the solid CH$_4$ may explain those data, but the mix would have to be tailored very specifically to simultaneously approach the large column densities of CH$_3$ and C$_2$H$_2$.

An alternative suggestion is to invoke turbulent chemistry, in which a high CH$^+$ abundance leads to enhancements of other hydrocarbons by 1-2 orders of magnitude (e.g. Hogerheijde et al. 1995, Joulain et al. 1998). However, the relative ratios of CH and CH$_3$ are unlikely to change in such models.

Given the detection of solid CH$_4$ and the low inferred temperatures, it is plausible that gas-solid interactions and grain-surface chemistry also play a role in producing the hydrocarbons. In this respect, the situation for CH$_3$ may be similar to that for NH in diffuse clouds (Mann & Williams 1984, van Dishoeck 1998). Conversion of atomic carbon to small hydrides on grain surfaces may be significant, but no model results exist yet for these conditions. Such models should also explain the C$_2$H$_2$ abundances and lack of complete C$_2$H$_2$ freeze-out. Alternatively, reactions of atomic H with PAHs and solid aliphatic hydrocarbon material, known to be present toward Sgr A* from the 3.4 μm absorption feature, may lead to CH$_3$. Shock chemistry is not likely to be important for this line of sight because of the low temperatures.
Future high spectral resolution observations of CH\textsubscript{3} toward Sgr A* to constrain the velocity structure, as well as observations of CH\textsubscript{3} and other molecules in different types of diffuse clouds are needed to constrain the basic hydrocarbon chemistry.

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Fig. 1.— (a),(b): Data and synthetic spectra of the CH$_3$ observations; (c): Determination of the CH$_3$ excitation temperature $T_{ex}$ from the integrated absorption ratio of the 16.0 $\mu$m $R(0)$ line and 16.5 $\mu$m Q-branch.

Fig. 2.— ISO spectra of Sgr A*: (a) LWS spectrum of the CH pure rotational line doublet; (b) SWS spectrum around the C$_2$H$_2$ $\nu_5$ Q-branch and the synthetic spectrum.
Table 1: Summary of results

| Molecule | Col. Dens. | $T_{ex}$ | Obs. Mode$^a$ |
|----------|-----------|---------|--------------|
| CH       | (1.1±0.1)$\times 10^{15}$ | 17$^b$ | LWS01 |
| CH$_3$   | (8.0±2.4)$\times 10^{14}$ | (17±2) | SWS06 |
| CH$_4$   | $\leq 1\times 10^{15}$ | 17$^b$ | SWS06 |
| C$_2$H$_2$ | (5.5±0.8)$\times 10^{14}$ | 17$^b$ | SWS06 |
| C$^{18}$O | (2.0±0.5)$\times 10^{16}$ | 8-13 | SWS06 |

$^a$ For details of the observing modes see de Graauw et al. (1996) and Clegg et al. (1996)

$^b$ Assumed excitation temperature
Table 2: Comparison of observed abundances with models

| Model     | CH    | CH$_3$ | CH$_4$ | C$_2$H$_2$ |
|-----------|-------|--------|--------|------------|
| Obs.      | 18$^{+22}_{-7}$(-9) | $13^{+22}_{-7}$(-9) | <17(-9) | $9^{+21}_{-4}$(-9) |
| LBH96$^b$ | 0.26(-9)  | 0.20(-9)  | 180(-9) | 15(-9)    |
| TH00$^c$  | 44(-9) | 8.6(-9) | 5.6(-9) | 9.2(-9)   |
| VDB00$^d$ | 3.2(-9) | 6.4(-9) | 18(-9) | 2.0(-9)   |

$^a$ All abundances with respect to H$_2$

$^b$ Lee et al. (1996) new standard model with $n_H = 10^4$ cm$^{-3}$ and $T=10$ K at steady state with low metal abundances

$^c$ Terzieva & Herbst (priv. comm.) translucent cloud model with $n_H = 2 \times 10^3$ cm$^{-3}$, $T=10$ K and $A_V=3$ mag at steady state with low metal abundances

$^d$ Updated models of van Dishoeck & Black (1986) and Jansen et al. (1995) for $n_H = 2 \times 10^3$ cm$^{-3}$ and $A_V=3$ mag at steady state with low metal abundances