Chemical Diversity in Three Massive Young Stellar Objects Associated with 6.7 GHz CH$_3$OH Masers

Kotomi Taniguchi$^{1,8}$, Masao Saito$^{2,3}$, Liton Majumdar$^4$, Tomomi Shimoikura$^5$, Kazuhito Dobashi$^5$, Hiroyuki Ozeki$^6$, Fumitaka Nakamura$^{2,3}$, Tomoya Hirota$^{2,3}$, Tetsuhiro Minamidani$^{2,7}$, Yusuke Miyamoto$^{2,9}$, and Hiroyuki Kaneko$^{10}$

1 Department of Astronomy, University of Virginia, Charlottesville, VA 22904, USA; k8pm@virginia.edu
2 Department of Astronomical Science, School of Physical Science, SOKENDAI (The Graduate University for Advanced Studies), Osawa, Mitaka, Tokyo 181-8588, Japan; kotomi.taniguchi@nao.ac.jp
3 National Astronomical Observatory of Japan (NAOJ), National Institutes of Natural Sciences (NINS), Osaka, Mitaka, Tokyo 181-8588, Japan
4 Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA
5 Department of Astronomy and Earth Sciences, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184-8501, Japan
6 Department of Environmental Science, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan
7 Nobeyama Radio Observatory, National Astronomical Observatory of Japan, (NAOJ), National Institutes of Natural Sciences (NINS), 462-2 Nobeyama, Minamimaki, Minamisaku, Nagano, 384-1305, Japan

Received 2018 April 13; revised 2018 August 28; accepted 2018 August 30; published 2018 October 23

Abstract

We have carried out observations in the 42–46 and 82–103 GHz bands with the Nobeyama 45 m radio telescope, and in the 338.2–339.2 and 348.45–349.45 GHz bands with the ASTE 10 m telescope, toward three high-mass star-forming regions containing massive young stellar objects (MYSOs), G12.89 +0.49, G16.86 −2.16, and G28.28 −0.36. We have detected HCN including its $^{13}$C and D isotopologues, CH$_3$OH, CH$_3$CCH, and several complex organic molecules. Using our previous results for HCN in these sources, we compare their N(HCN)/N(CH$_3$OH) ratios. The ratio in G28.28 −0.36 is derived to be 0.091 ± 0.039, which is higher than that in G12.89 +0.49 by one order of magnitude, and higher than in G16.86 −2.16 by a factor of ~5. We investigate the relationship between the N(HCN)/N(CH$_3$OH) and the N(CH$_3$CCH)/N(CH$_3$OH) ratios. The relationships of the two column density ratios in G28.28 −0.36 and G16.86 −2.16 are similar to each other, while HCN is less abundant compared to CH$_3$CCH in G12.89 +0.49. These results imply a chemical diversity in the lukewarm (T ∼ 20–30 K) envelope around MYSOs. In addition, several spectral lines from complex organic molecules, including very-high-excitation energy lines, have been detected toward G12.89 +0.49, while the line density is significantly low in G28.28 −0.36. These results suggest that organic-poor MYSOs are surrounded by a carbon-chain-rich lukewarm envelope (G28.28 −0.36), while organic-rich MYSOs, namely hot cores, are surrounded by a CH$_3$OH-rich lukewarm envelope (G12.89 +0.49 and G16.86 −2.16).

Key words: astrochemistry – ISM: molecules – stars: formation – stars: massive

1. Introduction

Molecules constitute a unique and powerful tool in astronomy. They provide an excellent diagnosis of the physical conditions and processes in the regions where they reside. Progress in this field, known as astrochemistry, is mainly driven by observations from various single-dish and interferometers at millimeter/submillimeter wavelengths along with space telescopes at mid- and far-infrared wavelengths (e.g., van Dishoeck 2018).

Unsaturated carbon-chain molecules tend to be abundant in young, low-mass starless cores and deficient in low-mass star-forming cores (Suzuki et al. 1992; Hirota et al. 2009), because they are mainly formed from ionized carbon (C$^+$) and atomic carbon (C) via ion–molecule reactions in the early stage of molecular clouds and destroyed mainly by reactions with oxygen atoms and depleting onto dust grains in the late stage. Carbon-chain molecules have been found to be abundant around two low-mass protostars: IRAS 04368+2557 in L1527 (Sakai et al. 2008) and IRAS 15398−3359 in Lupus (Sakai et al. 2009a). In these protostars, carbon-chain molecules are newly formed from CH$_3$ evaporated from dust grains in the lukewarm (T ∼ 20–30 K) gas (Sakai et al. 2008). This carbon-chain chemistry around the low-mass protostars was named warm carbon chain chemistry (WCCC; Sakai et al. 2008). The difference between hot corino chemistry and WCCC is considered to arise from the different timescale of the starless core phase; the long and short starless core phases lead to hot corino and WCCC sources, respectively (Sakai et al. 2008). Recently, sources possessing both hot corino and WCCC characteristics have been found and high spatial resolution observations showed that the spatial distributions of carbon-chain molecules and complex organic molecules (COMs) are different from each other (e.g., Imai et al. 2016).

Saturated COMs, organic species consisting of more than six atoms and being rich in hydrogen (Herbst & van Dishoeck 2009), are classically known to be abundant in the dense and hot ($n > 10^6$ cm$^{-3}$, $T \geq 100$ K) gas around young stellar objects (YSOs). COMs also have been found in the gas phase before ices thermally evaporates at temperatures above 100 K (Vastel et al. 2014). At these low temperatures, COMs can be desorbed from icy grain mantles via different types of non-thermal desorption processes such as: (1) the cosmic-ray desorption mechanism (Reboussin et al. 2014), (2) the chemical desorption mechanism (desorption due to the exothermicity of surface reactions; Garrod et al. 2007), and (3) photo-desorption (Rauad et al. 2016). The role of barrier-less gas phase reactions in forming COMs was also proposed recently by Balucani et al. (2015). Recent observations show the presence of some COMs, e.g., methylformate (HCOOCH$_3$), dimethyl ether (CH$_3$OCH$_3$), methyl cyanide (CH$_3$CN), and the complex radical methoxy...
(CH$_3$O) in regions where the dust temperature is less than 30 K, i.e., in pre-stellar cores (Bacmann et al. 2012; Vastel et al. 2014; Potapov et al. 2016) and cold envelopes of low-mass protostars (Oberg et al. 2010; Cernicharo et al. 2012; Jaber et al. 2014). Grain-surface chemistry certainly plays a role, for example, in forming hydrogenated species during the prestellar phase (Tielens & Hagen 1982; Caselli & Ceccarelli 2012), but not necessarily in the formation of all COMs.

New questions arise concerning the chemistry not only in the low-mass star-forming regions but also around massive young stellar objects (MYSOs). Fayolle et al. (2015) compared the chemistry between organic-poor and organic-rich MYSOs, namely hot cores. They suggested that hot cores are not required to form COMs, and temperature and initial ice composition possibly affect the complex organic distributions around MYSOs. Green et al. (2014) detected HC$_5$N, the second shortest of the cyanopolyynes (HC$_{2n+1}$N, $n = 1, 2, 3, \ldots$), in 35 hot cores associated with the 6.7 GHz methanol masers, which give us the exact positions of MYSOs (Urquhart et al. 2013). However, there remains the possibility that the emission of HC$_5$N comes from the outer cold molecular clouds or other molecular clouds in the large single-dish beam ($\sim$0/95). Taniguchi et al. (2017b) carried out observations toward four MYSOs where Green et al. (2014) detected HC$_5$N, using the Green Bank 100 m telescope (GBT) and the Nobeyama 45 m radio telescope. The four target sources were selected by adding the three criteria mentioned in Section 2 and we chose three sources showing the highest HC$_5$N peak intensities (G12.89+0.49, G16.86–2.16, and G28.28–0.36) and a source showing the low HC$_5$N peak intensity with the high CH$_3$CN peak intensities (G10.30–0.15). They detected the high excitation energy ($E_u/k \sim 100$ K) lines of HC$_5$N, which cannot be detected if HC$_5$N exists in the cold dark clouds, in the former three sources and confirmed that HC$_5$N exists in the warm gas around MYSOs. Therefore, carbon-chain molecules seem to be formed in the lukewarm gas around MYSOs, as well as WCCC sources in the low-mass star-forming regions. At present, we do not know the relationships between carbon-chain molecules and COMs around MYSOs.

In this paper, we report observational results in the 42–46, 82–103, 338.2–339.2, and 348.45–349.45 GHz bands obtained with the Nobeyama 45 m radio telescope and the Atacama Submillimeter Telescope Experiment (ASTE) 10 m telescope toward three MYSOs: G12.89+0.49, G16.86–2.16, and G28.28–0.36 (Section 3). We derive the rotational temperatures and beam-averaged column densities of HC$_5$N, CH$_3$OH, and CH$_3$CCH (Section 4). We compare the spectra and the chemical composition among the three sources, combining with previous HC$_5$N data (Taniguchi et al. 2017b), in order to investigate the relationship between carbon-chain species and COMs in high-mass star-forming regions (Section 5).

2. Observations

The observations presented in this paper were conducted in the Nobeyama 45 m radio telescope and the ASTE joint observation program (Proposal ID: J0161001, PI: Kotomi Taniguchi, 2016–2017 season). The observing parameters of each frequency band are summarized in Table 1. The Nobeyama 45 m telescope data were partly published in Taniguchi et al. (2017b).

The source selection criteria were described in Taniguchi et al. (2017b) as follows:

1. the source declination is above $-21^\circ$,
2. the distance (D) is within 3 kpc, and
3. CH$_3$CN was detected ($J_{mb, dv} > 0.5$ K km s$^{-1}$ for $J_K = 5_0 – 4_0$, line; Purcell et al. 2006).

Eight sources in the HC$_5$N-detected source list of Green et al. (2014) meet the above three criteria. We chose three out of the eight selected sources that show the highest peak intensities of HC$_5$N ($T_{mb} > 120$ mK). Table 2 summarizes the properties of our three target sources. The observed positions correspond to the 6.7 GHz methanol maser positions, which show the exact positions of the MYSOs (Urquhart et al. 2013).

2.1. Observations with the Nobeyama 45 m Radio Telescope

We carried out observations with the Nobeyama 45 m radio telescope from 2017 January to March. We employed the position-switching mode. The integration time was 20 s per on-source and off-source positions. The on-source positions are summarized in Table 2 and the off-source positions were set to be $+15^\circ$ away in declination. The total integration time was $\sim$1 hr and 2–4.5 hr in the 42–46 GHz and 82–103 GHz band observations, respectively.

The Z45 receiver (Nakamura et al. 2015) and the TZ receiver (Nakajima et al. 2013) were used in the observations at 42–46 GHz and 82–103 GHz, respectively. The main beam efficiency ($\eta_{mb}$) and the beam size (HPBW) at 43 GHz were 71% and 37$, respectively. The main beam efficiency and the beam size at 86 GHz were 54% and 18, respectively. The system temperatures were 120–150 K and 120–200 K during the observations at 42–46 GHz and 82–103 GHz, respectively. We used the SAM45 FX-type digital correlator (Kamazaki et al. 2012) in frequency settings whose bandwidths and resolutions were 500 MHz and 122.07 kHz for the Z45 observations, and 1000 MHz and 244.14 kHz for the TZ observations. The frequency resolutions corresponded to a velocity resolution of $\sim$0.85 km s$^{-1}$.

The telescope pointing was checked every 1.5 hr by observing the SiO maser line ($J = 1 - 1$, 43.12203 GHz) from OH39.7+1.5 at ($\alpha_{2000}$, $\delta_{2000}$) = (18$^h$56$^m$03$^s$, +06$^\circ$38$'$ 49$''$). We used the Z45 receiver for the pointing check during the 42–46 GHz band observations and the H40 receiver for the pointing check during the 82–103 GHz band observations. The pointing error was less than 3$''$.

The rms noises were 6–14 and 3–6 mK in the $T_A^*$ scale in the 42–46 GHz and 82–103 GHz bands, respectively. The baseline was fitted with a linear function. The absolute flux calibration error was approximately 10%.

2.2. Observations with the ASTE 10 m Telescope

The observations with the ASTE 10 m telescope were conducted in 2016 September and October. The DASH345 receiver and the WHSF FX-type digital spectrometer (Iguchi & Okuda 2008; Okuda & Iguchi 2008) were used. The observed frequency ranges were 338.2–339.2 and 348.45–349.45 GHz. The main beam efficiency and beam size were 60% and 22, respectively. The system temperatures were between 300 and 700 K, depending on the elevation and weather conditions. The frequency setting was 2048 MHz bandwidth and 1 MHz frequency resolution. The latter corresponded to 0.86 km s$^{-1}$, which is almost equal to that of the observations with the Nobeyama 45 m telescope. The total integration time was approximately 1–2.5 hr, with different times for each source.
### Table 1

| Frequency (GHz) | Telescope | Beam size (") | $\eta_{mb}$ (%) | $T_{sys}$ (K) | $\Delta\nu$ (kHz) | $T_{rms}$ (mK) |
|----------------|-----------|----------------|-----------------|--------------|-----------------|-------------|
| 42–46          | Nobeyama  | 37             | 71              | 120–150      | 122.07          | 6–14        |
| 82–103         | Nobeyama  | 18             | 54              | 120–200      | 244.14          | 3–6         |
| 338–349.4      | ASTE      | 22             | 60              | 300–700      | 1000            | 16–24       |

**Notes.**

- $a$ In $T_A^*$ scale.
- $b$ Values are at 86 GHz.

### Table 2

| Source         | R.A.$^a$ (J2000) | Decl.$^a$ (J2000) | $D$ (kpc) | $V_{LSR}$* (km s$^{-1}$) | Other Association$^b$ |
|----------------|------------------|-------------------|-----------|--------------------------|-----------------------|
| G12.89+0.49    | 18$^h$11$^m$51$^s$.4 | $-$17$^d$31$^m$30$^s$.9 | 2.50$^c$ | 33.3                      | N                     |
| G16.86–2.16    | 18$^h$29$^m$24$^s$.4 | $-$15$^d$16$^m$04$^s$.9 | 1.67$^d$ | 17.8                      | N                     |
| G28.28–0.36    | 18$^h$44$^m$13$^s$.3 | $-$04$^d$18$^m$03$^s$.9 | 3.0$^e$  | 48.9                      | Y                     |

**Notes.**

- $a$ Purcell et al. (2006).
- $b$ Values are at 86 GHz.
- $c$ Reid et al. (2014).
- $d$ Li et al. (2016).
- $e$ Green et al. (2014).
- $f$ Cyganowski et al. (2008).

We checked the telescope pointing every 2 hr by observing the $^{12}$CO ($J = 3 - 2$) line from W Aql at ($\alpha_{2000}$, $\delta_{2000}$) = (19$^h$15$^m$35$^s$.3, $-$07$^d$02$^m$50$^s$.3). The pointing error was less than 2".

The rms noise levels in the line-free regions were 23–24, 19–20, and 16–17 mK in $T_A^*$ scale in G12.89+0.49, G16.86–2.16, and G28.28–0.36, respectively. Some scans were excluded due to bad baselines. A linear fit was applied for baseline subtraction. The absolute flux calibration error was approximately 10%.

### 3. Results

We conducted data reduction using the Java Newstar software, the astronomical data analyzing system of both telescopes.

#### 3.1. Observational Results with the Nobeyama 45 m Radio Telescope

Figure 1 shows the spectra of the main isotopologue HC$_3$N and its $^{13}$C and D isotopologues in the three sources obtained with the Nobeyama 45 m radio telescope. We fitted the spectra with a Gaussian function and obtained the spectral line parameters as summarized in Table 3. Two rotational transitions, $J = 5 - 4$ and 10 – 9, of the main isotopologue are in the observed frequency bands, and they were detected from all three sources. The three $^{13}$C isotopologues were detected from G28.28–0.36 with a signal-to-noise ratio (S/N) above 4, HC$_3$CCCN was not detected in G12.89+0.49, whereas H$^{13}$CCCN was not detected in G16.86–2.16. DC$_3$N was detected in G28.28–0.36 with an S/N of 3 and in G16.86–2.16 with an S/N above 4. The $V_{LSR}$ values agree with the systemic velocities of each source (Table 2).

The line profiles of the main isotopologue show wing emission, suggesting that HC$_3$N also exists in the molecular outflow (e.g., Shimajiri et al. 2015; Taniguchi et al. 2018). This wing emission is most prominent in G16.86–2.16, where the blue and red components are clearly detected. The red and blue components are prominent in G12.89+0.49 and G28.28–0.36, respectively. These features of the wing emission of HC$_3$N are similar to those of CH$_3$OH (Figure 3), as mentioned below. Hence, this origin of molecular outflows is plausible.

Figure 2 shows the spectra of CH$_3$CCH obtained with the Nobeyama 45 m radio telescope. Its $J = 5 - 4$ and 6 – 5 $K$-ladder lines ($K = 0 - 0$, 1 – 1, 2 – 2, and 3 – 3) were detected from the three sources with an S/N above 4. We fitted the spectra with four-component Gaussian profiles. We fixed the centroid velocities to be the systemic velocities for each source (Table 2). The spectral line parameters are summarized in Table 4. There is no presence of wing emission in the CH$_3$CCH spectra and the lines are well fitted with the Gaussian profile.

Nine thermal CH$_3$OH lines were detected from G12.89+0.49, and eight lines, apart from the 6 – 2.5 – 7 – 1.7 $E$ transition, were detected from the other two sources with an S/N above 4 as shown in Figure 3. We fitted the spectra with Gaussian profiles and the spectral line parameters are summarized in Table 5. For the four lines shown in the top panels of Figure 3, we applied four-component Gaussian fitting. In the same way as for CH$_3$CCH, the centroid velocities were fixed to be the systemic velocities of each source (Table 2). Wing emission for the red and blue velocity components is seen in G16.86–2.16, while...
only the red component is found in G12.89+0.49. In G28.28−0.36, no wing emission is seen, which may be due to its lower line intensities.

Figures 4 and 5 show the spectra in the frequency bands covered with the TZ receiver. Several lines from COMs have been detected with an S/N above 4. An analysis of the COMs
Table 3
Spectral Line Parameters of the Main Isotopologue HC$_3$N and Its $^{13}$C and D Isotopologues in the Three Sources with the Nobeyama 45 m Telescope

| Species Transition | Frequency (GHz) | $E_u/k$ (K) | $T_{mb}$ (K) | FWHM (km s$^{-1}$) | $\int T_{mb} dv$ (K km s$^{-1}$) | $V_{LSR}$ (km s$^{-1}$) |
|--------------------|----------------|-------------|--------------|-------------------|-----------------------------|----------------|
| HC$_3$N            | 45.490314      | 6.5         | 1.64 (4)     | 3.35 (9)          | 5.8 (2)                     | 32.8          |
| $J = 10 - 9$       | 90.979023      | 24.0        | 2.58 (12)    | 4.1 (2)           | 11.3 (8)                    | 32.5          |
| H$^{13}$CCN        | 44.084172      | 6.4         | 0.037 (7)    | 3.0 (7)           | 0.12 (4)                    | <0.036        |
| $J = 5 - 4$        | 45.2973345     | 6.5         | <0.027       | ...               | ...                         | ...           |
| HCC$_{13}$CN       | 45.3017069     | 6.5         | 0.042 (7)    | 3.4 (7)           | 0.15 (4)                    | 32.5          |
| DC$_3$N            | 101.314818     | 31.6        | <0.013       | ...               | ...                         | ...           |

Notes. Numbers in parentheses are the standard deviation of the Gaussian fit, expressed in units of the last significant digit. For example, 1.64 (4) means 1.64 ± 0.04. The upper limits correspond to the 3σ limits.

a Taken from the Cologne Database for Molecular Spectroscopy (CDMS; Müller et al. 2005).

b The errors are 0.85 km s$^{-1}$, which corresponds to the velocity resolution (Section 2.1).
requires the simultaneous fitting of multiple species to avoid blending effects with other lines. In our case, the detected COMs have similar excitation energy and such fitting cannot degenerate excitation temperatures and column densities. Therefore, we cannot derive their rotational temperatures and column densities accurately and we will not discuss these COMs in the rest of this paper. We summarize the detection and non-detection of COMs in each source in Table 6. G12.89 +0.49 is the most line-rich source with strong peak intensities, and both nitrogen-bearing COMs and oxygen-bearing COMs have been detected. On the other hand, only CH3OH and CH3CHO were detected with weak peak intensities in G28.28−0.36.

3.2. Observational Results with the ASTE 10 m Telescope

Figure 6 shows the spectra in the 338.2–339.2 and 348.45–349.45 GHz bands obtained with the ASTE 10 m telescope. Table 7 summarizes the spectral line parameters obtained from the Gaussian fitting. The detection limit was set at an S/N above 4. The $V_{LSR}$ values are consistent with the systemic velocities of each source (Table 2).\textsuperscript{10} Several high-excitation energy ($E_u/k > 200$ K) lines from CH$_3$OH and CH$_3$CN were detected from G12.89 +0.49. On the other hand, only two lower-excitation energy ($E_u/k < 75$ K) lines of CH$_3$OH and CCH were detected from G28.28−0.36. The line density in G16.86−2.16 is between those in G12.89+0.49 and G28.28−0.36. The relatively high-excitation energy line of CH$_3$OH ($\tilde{7}_{4,3}−\tilde{6}_{4,2}$ $A^+$ transition; $E_u/k = 145.3$ K) was detected in G16.86−2.16. The results suggest that hot gas exists in G12.89+0.49 and G16.86−2.16, which is supported by the detection of the metastable inversion transition NH$_3$ lines with the very high excitation energies, $(J, K) = (8, 8)$ at

\textsuperscript{10} The $V_{LSR}$ values of molecular emission lines are shifted by $\sim$0.2 km s$^{-1}$ due to bug in ASTE Newstar. The results and discussions in this paper are not affected.
26.51898 GHz ($E_u/k = 686$ K) and $(J, K) = (9, 9)$ at 27.47794 GHz ($E_u/k = 852$ K), with the GBT (Taniguchi et al. 2017b).

In G12.89+0.49 and G16.86−2.16, the line profiles of CH$_3$OH show wing emission suggestive of molecular outflow origins. In addition, the line widths (FWHM) of

Figure 3. Spectra of CH$_3$OH in the three sources. The red lines show the Gaussian fitting results and the gray vertical lines show the systemic velocity for each source.
### Table 5

Spectral Line Parameters of CH$_3$OH in the Three Sources with the Nobeyama 45 m Telescope

| Transition | Frequency$^a$ (GHz) | $E_u/k$ (K) | $T_{mb}$ (K) | FWHM (K km s$^{-1}$) | $\int T_{mb}dv$ (K km s$^{-1}$) | $V_{LSR}$ (km s$^{-1}$) |
|------------|---------------------|-------------|--------------|----------------------|-------------------------------|-------------------------|
| 5$_{-1.5}$ - 4$_{1.4}$E | 84.521169 | 40.4 | 1.97 (8) | 3.44 (14) | 7.2 (4) | 32.5 |
| 6$_{-2.5}$ - 7$_{-1.7}$E | 85.568084 | 74.7 | 0.206 (7) | 5.06 (17) | 1.11 (5) | 32.9 |
| 8$_{0.8}$ - 7$_{1.7}$A$^+$ | 95.169463 | 83.5 | 1.82 (7) | 3.70 (15) | 7.2 (4) | 32.4 |
| 2$_{4.2}$ - 1$_{1.1}$A$^+$ | 95.914309 | 21.4 | 0.664 (13) | 4.39 (10) | 3.10 (9) | 32.7 |
| 2$_{-1.1}$ - 1$_{-1.1}$E | 96.739362 | 12.5 | 1.81 (2) | 4.09 (6) | 7.87 (15) | ... |
| 2$_{4.2}$ - 1$_{0.1}$A$^+$ | 96.741375 | 7.0 | 2.39 (2) | 3.60 (4) | 9.14 (14) | ... |
| 2$_{4.2}$ - 1$_{0.1}$E | 96.744550 | 20.1 | 0.99 (2) | 4.40 (11) | 4.66 (15) | ... |
| 2$_{4.1}$ - 1$_{1.0}$E | 96.755511 | 28.0 | 0.64 (2) | 4.47 (17) | 3.06 (15) | ... |
| 2$_{4.1}$ - 1$_{1.0}$A$^+$ | 97.582804 | 21.6 | 0.702 (12) | 4.18 (8) | 3.12 (8) | 32.7 |

Notes. Numbers in parentheses are the standard deviation of the Gaussian fit, expressed in units of the last significant digits. The upper limits correspond to the 3σ limits.

$^a$ Taken from CDMS (Müller et al. 2005).

$^b$ The errors are 0.85 km s$^{-1}$, which corresponds to the velocity resolution (Section 2.1).
CH$_3$OH in these two sources (∼5–6 km s$^{-1}$) are larger than those in G28.28−0.36 (∼2–3 km s$^{-1}$). This may suggest that CH$_3$OH in G28.28−0.36 exists in less turbulent regions, as discussed in more detail in Section 5.6.

4. Analyses

4.1. Rotational Diagram Analysis

We derived the rotational temperatures and beam-averaged column densities of HC$_3$N, CH$_3$CCH, and CH$_3$OH with a beam size of 18″ in the three sources from rotational diagram analysis, using the following formula (Goldsmith & Langer 1999):

$$\ln \frac{3k \int T_{mb} dv}{8\pi \gamma S \mu^2} = \ln \frac{N}{Q(T_{rot})} - \frac{E_u}{kT_{rot}}. \quad (1)$$

where $k$ is the Boltzmann constant, $S$ is the line strength, $\mu$ is the permanent electric dipole moment, $N$ is the column density, and $Q(T_{rot})$ is the partition function. The permanent electric dipole moments are 3.7312, 0.784, and 0.899 D for HC$_3$N, CH$_3$CCH, and CH$_3$OH, respectively. We used the $\int T_{mb} dv$ values summarized in Tables 3–5.
Figure 7 shows the fitting results of HC$_3$N, CH$_3$CCH, and CH$_3$OH in the three sources. The errors include the Gaussian fitting errors, the uncertainties from the main beam efficiency of 10%, from the chopper-wheel method of 10%, and a pointing calibration error of 30%. The derived rotational temperatures and column densities are summarized in Table 8.

In the case of HC$_3$N, we added data of the $J=3-2$ transition obtained with the GBT (Table 3 in Taniguchi et al. 2017b). The beam sizes are different for the three transitions: 27\''', 37\'''', and 18\''' for $J=3-2$, 5-4, and 10-9, respectively. Assuming a small beam filling factor, we multiplied the integrated intensities of the GBT data by $\left(\frac{27''}{18''}\right)^2$.

**Table 6** Summary of Detection of Complex Organic Molecules in the Three Sources with the Nobeyama 45 m Telescope

| Species      | G12.89+0.49 | G16.86-2.16 | G28.28-0.36 |
|--------------|-------------|-------------|-------------|
| CH$_3$OCHO   | Y           | Y           | N           |
| CH$_3$CH$_2$OH | Y         | N           | N           |
| CH$_3$CHO    | Y           | Y           | Y           |
| CH$_3$OCH$_3$ | Y           | N           | N           |
| NH$_2$CHO    | Y           | N           | N           |
| CH$_3$CHCN   | Y           | N           | N           |
| CH$_3$CH$_2$CN | Y       | N           | N           |

**Note.** “Y” and “N” represent detection and non-detection with an S/N above 4.
and the 45 GHz band data by $\sqrt{37^\circ}$ for the correction of the different beam sizes (filled circles in Figure 7). The red lines are the best-fitting results for $J = 5 - 4$ without beam size correction and $J = 10 - 9$ transitions, and the green lines show the fitting results for the three transitions with beam size correction. In the case of the fitting for the $J = 5 - 4$ and $10 - 9$ transitions, the $\sigma$ fluctuation in the integrated intensity causes unlikely large errors in the derived rotational temperature and column density (e.g., $T_{\text{rot}} \sim 600$ K), and we do not include these errors in Table 8. All of the three transitions are better fitted with beam size correction. The fitting results imply that the spatial distribution of HC$_3$N is smaller than 18$''$, corresponding to ~0.07–0.1 pc radii at the source distances (Table 2), as in the case for HC$_5$N (Taniguchi et al. 2017b); they derived the rotational temperatures of HC$_5$N with beam size correction to be $\sim 13$–$20$ K in the three sources. The different rotational temperatures between HC$_3$N and HC$_5$N probably arise from the fact that we observed only lower excitation energy lines ($E_u/k < 24.0$ K), compared to HC$_5$N ($E_u/k \leq 100$ K; Taniguchi et al. 2017b), and the presence of complex excitation conditions.

In the case of CH$_3$CCH, we multiplied the integrated intensities of the $J = 6 - 5$ transition lines by $\left(\frac{85.4 \text{ GHz}}{102.5 \text{ GHz}}\right)^2$ in order to correct the values for the 18$''$ beam size at the 85 GHz band in G12.89+0.49 and G16.86−2.16, because the data for the $J = 6 - 5$ transition are systematically higher than those for the $J = 5 - 4$ transition. In Figure 7, open and filled circles represent the integrated intensities without and with frequency dependence correction of the beam size, respectively. The black lines show the fitting results with correction of frequency dependence. All of the data can be fitted simultaneously, which means that the spatial distribution of CH$_3$CCH is smaller than 18$''$. This is the same as for HC$_3$N and HC$_5$N. The derived rotational temperatures are $33^{+20}_{-9}$, $29^{+15}_{-14}$, and $23^{+9}_{-8}$ K in G12.89+0.40, G16.86−2.16, and G28.28−0.36, respectively.
### Table 7

Spectral line Parameters in the Three Sources with the ASTE 10 m Telescope

| Species Transition | Frequency (GHz) | $E_u/E_k$ (K) | $T_{mb}$ (K) | FWHM (km s$^{-1}$) | $\int T_{mb}dv$ (K km s$^{-1}$) | $V_{lsr}$ (km s$^{-1}$) | $T_{mb}$ (K) | FWHM (km s$^{-1}$) | $\int T_{mb}dv$ (K km s$^{-1}$) | $V_{lsr}$ (km s$^{-1}$) |
|--------------------|-----------------|---------------|--------------|-------------------|-------------------------------|---------------------|--------------|-------------------|-------------------------------|---------------------|
| SO$_2$ 18,14 – 18,15 | 338.305993 | 196.8 | 0.13 (4)$^d$ | 5.9 (9) | 0.81 (9) | 33.1 | <0.09 | ... | ... | ... |
| CH$_3$OH | 7,17 – 6,16 E | 338.344628 | 70.5 | 1.23 (4) | 4.6 (9) | 5.99 (10) | 32.9 | 0.82 (3) | 4.5 (9) | 3.94 (8) | 17.3 |
| | 7,07 – 6,06 A$^+$ | 338.408681 | 65.0 | 1.50 (4) | 5.1 (9) | 8.06 (11) | 33.0 | 1.07 (3) | 4.8 (9) | 5.42 (7) | 17.2 |
| | 7,61 – 6,50 A$^+$ | 338.430933 | 253.9 | 0.23 (4) | 5.8 (9) | 1.40 (9) | 32.9 | <0.09 | ... | ... | ... |
| | 7,52 – 6,43 E | 338.442344 | 258.7 | 0.26 (4) | 4.5 (9) | 1.22 (9) | 33.0 | <0.09 | ... | ... | ... |
| | 7,53 – 6,42 E | 338.456499 | 189.0 | 0.26 (4) | 5.0 (9) | 1.38 (11) | 32.9 | <0.09 | ... | ... | ... |
| | 7,33 – 6,23 A$^+$ | 338.475290 | 201.1 | 0.25 (4) | 5.2 (9) | 1.42 (11) | 32.7 | <0.09 | ... | ... | ... |
| | 7,33 – 6,22 A$^+$ | 338.486337 | 202.9 | 0.25 (4) | 5.9 (9) | 1.55 (11) | 33.2 | <0.09 | ... | ... | ... |
| | 7,44 – 6,33 E | 338.504099 | 152.9 | 0.30 (4) | 6.0 (9) | 1.91 (10) | 32.8 | <0.09 | ... | ... | ... |
| | 7,43 – 6,22 A$^+$ | 338.512627 | 145.3 | 0.51 (4) | 4.7 (9) | 2.56 (11) | 32.7 | 0.14 (3) | 6.1 (9) | 0.92 (10) | 17.7 |
| | 7,33 – 6,13 E | 338.530249 | 161.0 | 0.27 (4) | 6.0 (9) | 1.72 (9) | 32.8 | <0.09 | ... | ... | ... |
| | 7,33 – 6,12 A$^+$ | 338.540795 | 114.8 | 0.56 (4) | 6.1 (9) | 3.64 (12) | 32.0 | 0.15 (3) | 6.7 (9) | 1.10 (10) | 16.1 |
| | 7,33 – 6,32 A$^+$ | 338.559928 | 127.7 | 0.36 (4) | 4.5 (9) | 1.73 (10) | 32.8 | <0.09 | ... | ... | ... |
| | 7,33 – 6,21 E | 338.583195 | 112.7 | 0.36 (4) | 5.2 (9) | 2.00 (10) | 33.0 | <0.09 | ... | ... | ... |
| | 7,61 – 6,43 E | 338.614999 | 86.1 | 0.73 (4) | 5.5 (9) | 4.28 (11) | 33.3 | 0.26 (3) | 4.3 (9) | 1.20 (8) | 17.3 |
| | 7,52 – 6,34 A$^+$ | 338.639939 | 102.7 | 0.45 (4) | 4.9 (9) | 2.36 (11) | 33.2 | 0.12 (3) | 5.8 (9) | 0.72 (9) | 17.9 |
| 14,13 – 14,14 A$^+$ | 338.72294 | 90.9 | 0.89 (4) | 4.9 (9) | 4.64 (11) | 32.3 | 0.51 (3) | 5.8 (9) | 3.10 (7) | 18.2 |
| CH$_3$OH | 13,01 – 12,12 A$^+$ | 338.759948 | 205.9 | 0.17 (4) | 4.5 (9) | 0.80 (6) | 33.0 | <0.09 | ... | ... | ... |
| H$_2$CS | 10,0 – 9,1,8 | 348.534367 | 105.2 | 0.55 (4) | 4.5 (9) | 2.64 (11) | 32.9 | 0.10 (3) | 6.2 (9) | 0.64 (6) | 17.4 |
| CCH | N = 4 – 3, J = 9/2 – 7/2 | 349.3374558 | 41.9 | 1.17 (4) | 4.2 (9) | 5.22 (11) | 33.7 | 1.12 (3) | 3.2 (9) | 3.82 (8) | 16.8 |
| | N = 4 – 3, J = 7/2 – 5/2 | 349.3992738 | 41.9 | 0.80 (4)$^e$ | 3.8 (9) | 3.27 (11) | 32.1 | 0.86 (3) | 3.3 (9) | 3.04 (8) | 17.1 |
| CH$_3$CN | J$_K$ = 19$_K$ – 18$_K$ | 349.2123106 | 424.7 | 0.14 (4) | 5.4 (9) | 0.81 (12) | 33.1 | <0.09 | ... | ... | ... |
| | J$_K$ = 19$_K$ – 18$_K$ | 349.2860057 | 346.2 | 0.16 (4) | 5.8 (9) | 0.98 (12) | 33.9 | <0.09 | ... | ... | ... |
| | J$_K$ = 19$_K$ – 18$_K$ | 349.3463428 | 282.0 | 0.20 (4)$^f$ | 5.1 (9) | 1.07 (11) | 33.3 | <0.09 | ... | ... | ... |
| | J$_K$ = 19$_K$ – 18$_K$ | 349.4268497 | 196.3 | 0.23 (4) | 5.3 (9) | 1.32 (11) | 33.0 | <0.09 | ... | ... | ... |

Notes. Numbers in parentheses are the standard deviation, expressed in units of the last significant digits. The upper limits correspond to the 3σ limits.

$^a$ Taken from CDMS (Müller et al. 2005).

$^b$ The errors were derived using the following formula: $\Delta T_{mb} = \sqrt{n} \Delta v$, where $\Delta T_{mb}$, $n$, and $\Delta v$ are the rms noise in the emission-free regions, the number of channels, and velocity resolution per channel, respectively.

$^c$ Tentative detection with S/N above 3.

$^d$ These lines are contaminated and fitting results are tentative.
Figure 7. Rotational diagram of HC$_3$N, CH$_3$CCH, and CH$_3$OH in the three sources. HC$_3$N (upper panels): the filled and open circles represent results with and without beam size correction, respectively. The red line is the fitting results for the $J = 5 - 4$ data without beam size correction and $J = 10 - 9$ data. The green line shows the fitting results for all of the lines with the beam size correction. CH$_3$CCH (middle panels): the filled and open circles represent results with and without frequency dependence correction, respectively. The black lines show the fitting results with this correction. CH$_3$OH (lower panels): the black lines show the fitting results for all of the observed lines.

Table 8
The Rotational Temperatures and Beam-averaged Column Densities of HC$_3$N, CH$_3$CCH, and CH$_3$OH

| Species | $T_{\text{rot}}$ (K) | $N$ (cm$^{-2}$) | $T_{\text{rot}}$ (K) | $N$ (cm$^{-2}$) | $T_{\text{rot}}$ (K) | $N$ (cm$^{-2}$) |
|---------|---------------------|----------------|---------------------|----------------|---------------------|----------------|
| HC$_3$N |                     |                |                     |                |                     |                |
| $J = 5 - 4$ & $10 - 9$ | 24 | $4.4 \times 10^{13}$ | 20 | $4.3 \times 10^{13}$ | 13.4 | $2.0 \times 10^{13}$ |
| All     | $7.7^{+1.6}_{-2.8}$ | $(1.4 \pm 0.3) \times 10^{14}$ | $7.2^{+1.4}_{-2.4}$ | $(1.3 \pm 0.3) \times 10^{14}$ | $6.2^{+1.1}_{-1.7}$ | $(7.6 \pm 2.1) \times 10^{13}$ |
| CH$_3$CCH | $33^{+3.0}_{-2.9}$ | $1.0^{+0.11}_{-0.11} \times 10^{15}$ | $29^{+1.5}_{-1.5}$ | $5.4^{+0.3}_{-0.3} \times 10^{14}$ | $23^{+2.2}_{-3.2}$ | $3.7^{+0.5}_{-0.4} \times 10^{14}$ |
| CH$_3$OH | $42^{+3.3}_{-3.1}$ | $2.9^{+0.2}_{-0.2} \times 10^{15}$ | $36^{+1.8}_{-1.5}$ | $1.5^{+0.2}_{-0.3} \times 10^{15}$ | $18^{+3.5}_{-3.2}$ | $2.3^{+0.5}_{-0.4} \times 10^{14}$ |

Note. The errors represent the standard deviation.
In the case of CH$_3$OH, we fitted the data using all the lines in the 85–98 GHz band summarized in Table 5, and the fitting results are shown by the black lines in Figure 7. As in the case for CH$_3$CCH, we derived beam-averaged column densities a beam size of 18", correcting the frequency dependence of the beam size by multiplying the integrated intensities of the lines in the 95–98 GHz band summarized in Table 5, and the rotational temperatures of CH$_3$OH to be 5 ± 5 K. We used the rotational temperatures of HC$_3$N summarized in Table 8 as the excitation temperatures. We calculated two cases of excitation temperature (Table 8) for each source. J(T) in Equation (3) is the effective temperature equivalent to that in the Rayleigh–Jeans law. In Equation (4), N is the column density, $\Delta \nu$ is the line width (FWHM, Table 3), Q is the partition function, $\mu$ is the permanent electric dipole moment, and $\epsilon_{\text{lower}}$ is the energy of the lower rotational energy level. The electric dipole moments are 3.7408 D and 3.73172 D for DC$_3$N and the three $^{13}$C isotopologues, respectively. The derived column densities and the D/H and $^{12}$C/$^{13}$C ratios are summarized in Table 9.

### 5. Discussion

In this section, we will discuss comparisons of the chemical composition among MYSOs using CH$_3$OH, CH$_3$CCH, and HC$_3$N, all of which are considered to be in lukewarm envelopes (Table 8). We assume that the spatial distributions of CH$_3$OH, CH$_3$CCH, and HC$_3$N are similar to each other. This assumption is based on the following results: the source sizes of both HC$_3$N and CH$_3$CCH seem to be smaller than 18" (see Taniguchi et al. 2017b and Section 4.1), and the rotational temperatures of CH$_3$OH are comparable with those of CH$_3$CCH in our three sources. Nitrogen-bearing COMs usually originate from hot cores (e.g., Bisschop et al. 2007), and thus we do not include them in the discussion. We will also discuss the relationship between the line width and excitation energy of rotational lines of CH$_3$OH.

#### 5.1. Comparisons of Fractional Abundances in High-mass Star-forming Regions

We derived the fractional abundances of HC$_3$N, CH$_3$OH, and CH$_3$CCH, $X(a) = N(a)/N(H_2)$, in the three sources. Their $N(H_2)$ column densities, $N(H_2)$, were derived by Taniguchi et al. (2017b). The $N(H_2)$ values and fractional abundances of HC$_3$N,
CH$_3$OH, CH$_3$CCH, and HC$_5$N are summarized in Table 10. The derived $X$(CH$_3$OH) values are $1.2^{+1.8}_{-1.0} \times 10^{-7}$, $8.8^{+5.3}_{-6.3} \times 10^{-8}$, and $4.6^{+7.0}_{-3.4} \times 10^{-8}$ in G12.89+0.49, G16.86−2.16, and G28.28−0.36, respectively. The $X$(CH$_3$CCH) values are derived to be $4.2^{+2.2}_{-0.9} \times 10^{-8}$, $3.2^{+1.9}_{-1.5} \times 10^{-8}$, and $7.6^{+5.2}_{-4.4} \times 10^{-8}$. We derive the $X$(HC$_3$N) values for two cases, fitting the results of two transitions and all transitions (Table 8). Figure 8 shows the fractional abundances in the three sources. All of the column densities including molecular hydrogen were derived as beam-averaged values for a beam size of 18″. More accurate column densities and fractional abundances can be obtained in the future via interferometric observations that resolve the size of the sources.

Although our sample is small, there seems to be an anti-correlation between $X$(CH$_3$OH) and $X$(HC$_3$N). G12.89+0.49 shows the highest $X$(CH$_3$OH) value and the lowest $X$(HC$_3$N) value among the three sources, while G28.28−0.36 shows the lowest $X$(CH$_3$OH) value and the highest $X$(HC$_3$N) value. We further discuss the relationship between HC$_3$N and CH$_3$OH in Section 5.2. $X$(HC$_3$N) has a positive correlation with $X$(HC$_3$N) and a negative correlation with $X$(CH$_3$OH).

The $X$(CH$_3$CCH) values in the three sources are consistent within their 1σ errors, and we cannot find any clear correlations between HC$_3$N and CH$_3$CCH. According to the gas–grain–bulk three-phase chemical network simulation (Majumdar et al. 2016, 2017a, 2017b), assuming that the temperatures are 20 and 30 K and the density is $10^5$ cm$^{-3}$, CH$_3$CCH is formed on the grains and desorbed non-thermally (Herbst 1993; Garrod et al. 2007). HC$_5$N is formed in the gas phase mainly by the neutral–neutral reaction of CN + C$_3$H$_2$ and the electron recombination reaction of H$_2$C$_3$N$^+$. The neutral–neutral reaction is also a main formation pathway to HC$_5$N in the model of Chapman et al. (2009). They suggested that C$_3$H$_2$ is formed by the reaction of C$_2$H$_2$ + CCH. C$_3$H$_2$ can be formed in the gas phase from CH$_4$ (Hassel et al. 2008) and can be directly evaporated from grain mantles (Lahuiss & van Dishoeck 2000). Hence, the production of CH$_3$CCH and HC$_5$N seems to be related to the grain–surface reactions even in lukewarm envelopes ($T \sim 20–30$ K). The lack of correlation between CH$_3$CCH and HC$_5$N may imply that there is no direct relationship between them, which is also indicated in the chemical network simulation.

5.2. Variety of the N(HC$_3$N)/N(CH$_3$OH) Ratio

Taniguchi et al. (2017b) found that the N(HC$_3$N)/N(CH$_3$OH) ratio, where $W$ represents the integrated intensity, varies by more than one order of magnitude among the three sources, and suggested the possibility of chemical differentiation. In this paper, we derived the CH$_3$OH column densities and then calculated the N(HC$_3$N)/N(CH$_3$OH) ratios in the observed three sources, as shown in Figure 9. We also added the data toward the high-mass protostellar object NGC2264 CMM3 (Watanabe et al. 2015). Watanabe et al. derived N(HC$_3$N) and N(CH$_3$OH) to be $(2.5 \pm 0.9) \times 10^{13}$ cm$^{-2}$ and $(1.8 \pm 0.2) \times 10^{15}$ cm$^{-2}$, respectively. We took the cold component value for CH$_3$OH, because its rotational temperature (24.3 ± 2.6 K) is comparable.

![Figure 8](image-url) Fractional abundances of CH$_3$OH, CH$_3$CCH, HC$_3$N, and HC$_5$N in the high-mass star-forming regions. The HC$_3$N values are taken from Taniguchi et al. (2017b).

### Table 10

| Source     | $N$(H$_2$) (×10$^{23}$ cm$^{-2}$) | $X$(CH$_3$OH) (×10$^{-9}$) | $X$(CH$_3$CCH) (×10$^{-9}$) | $X$(HC$_3$N$^a$) (×10$^{-9}$) | $X$(HC$_5$N$^b$) (×10$^{-9}$) | $X$(HC$_5$N$^c$) (×10$^{-16}$) |
|------------|---------------------------------|---------------------------|-----------------------------|-------------------------------|-------------------------------|-------------------------------|
| G12.89+0.49| 2.4$^{+2.5}_{-0.3}$            | 12$^{+18}_{-6.3}$         | 4.2$^{+2.2}_{-0.9}$         | 1.8 ± 0.9                     | 5.8$^{+4.3}_{-3.6}$           | 9.9$^{+5.4}_{-3.4}$          |
| G16.86−2.16| 1.7$^{+1.9}_{-0.1}$            | 8.8$^{+11}_{-3.8}$        | 3.2$^{+1.9}_{-1.5}$         | 2.5$^{+1.1}_{-0.9}$           | 7.7$^{+5.7}_{-3.9}$           | 16 ± 7                       |
| G28.28−0.36| 0.49$^{+0.42}_{-0.16}$         | 4.6$^{+7.0}_{-3.4}$       | 7.6$^{+5.2}_{-4.4}$         | 4.1$^{+2.0}_{-1.9}$           | 16$^{+14}_{-9.5}$             | 42$^{+26}_{-20}$             |

Notes. The errors represent the standard deviation. These values are averaged with a beam size of 18″.

$^a$ Taniguchi et al. (2017b).

$^b$ The HC$_3$N column densities were derived from $J = 5 − 4$ and $10 − 9$.

$^c$ The HC$_3$N column densities were derived from three rotational transitions.
Figure 9. Comparison of the \(N(\text{HC}_5\text{N})/N(\text{CH}_3\text{OH})\) ratio among the three high-mass star-forming regions. The data for NGC2264 CMM3 were taken from Watanabe et al. (2015).

Figure 10. Plot of \(N(\text{CH}_3\text{CCH})/N(\text{CH}_3\text{OH})\) vs. \(N(\text{HC}_5\text{N})/N(\text{CH}_3\text{OH})\). The data for NGC2264 CMM3 were taken from Watanabe et al. (2015). The labels of G12, G16, G28, and NGC2264 indicate the plots for G12.89+0.49, G16.86−2.16, G28.28−0.36, and NGC2264 CMM3, respectively.

These results suggest chemical diversity in the lukewarm envelope.

5.4. Relationship of the Chemical Composition between the Central Core and Envelope

He et al. (2012) carried out 1 mm spectral line survey observations toward 89 GLIMPSE Extended Green Objects (EGOs; Cyganowski et al. 2008). From their survey observations, there are largely two types of EGO clouds; line-rich and line-poor sources. It is unclear why some sources show line-poor spectra, and others show many lines of COMs. Ge et al. (2014) suggested that the EGO cloud cores are possibly in the short onset phase of the hot core stage, when \(\text{CH}_3\text{OH}\) ice is quickly evaporating from grain surfaces at a gas temperature of ~100 K. Hence, the difference between the line-poor and line-rich EGO cloud cores seems to originate from chemical differentiation rather than chemical evolution. Fayolle et al. (2015) compared the chemistry between organic-poor and organic-rich MYSOs (hot cores), but the relationship between the central core and the envelope was not clear. In this subsection, we discuss the possibility of a relationship of the chemical composition between the core and the envelope.

There are clear differences in the spectra of the three sources (Figures 4−6). As summarized in Table 6, the detected COMs are different. \(\text{CH}_3\text{CHO}\) was detected toward all three sources, and is considered to exist in the envelope (Fayolle et al. 2015). In G12.89+0.49, the largest number of COMs were detected, while G28.28−0.36 is a line-poor source. The results in G28.28−0.36 are consistent with those of He et al. (2012), showing that only \(\text{H}^3\text{C}^+\) was detected. As discussed in Section 5.2, the \(N(\text{HC}_5\text{N})/N(\text{CH}_3\text{OH})\) ratio in G28.28−0.36 is higher than that in G12.89+0.49 by an order of magnitude. In the case of G16.86−2.16, the \(N(\text{HC}_5\text{N})/N(\text{CH}_3\text{OH})\) ratio shows a value between those of G12.89+0.49 and G28.28−0.36, and the line density and the COM’s line intensities are also between these. From these results, the line-poor MYSOs are likely to be surrounded by a carbon-chain-rich envelope, while the line-rich MYSOs, i.e., hot cores, appear to be surrounded by a \(\text{CH}_3\text{OH}\)-rich envelope.
5.5. Isotopic Fractionation of $^7$H$_3$N

The $^{12}C/^{13}C$ ratio shows a gradient with distance from the Galactic center ($D_{GC}$; e.g., Savage et al. 2002; Milam et al. 2005). Recent observations derived the following relationship (Haffen et al. 2017):

$$^{12}C/^{13}C = 5.21(\pm 0.52)D_{GC} + 22.6(\pm 3.3),$$  \hspace{1cm} (5)

where $D_{GC}$ is in units of kpc. We estimated the $D_{GC}$ values of each source using trigonometry; these are estimated at 5.8 and 8.9 kpc for G12.89+0.49 and G16.86–2.16, respectively. The $D_{GC}$ value of G28.28–0.36 was derived to be 5.4 kpc by Taniguchi et al. (2016b). From Equation (5), the $^{12}C/^{13}C$ ratios are calculated as 53 ± 6, 69 ± 8, and 51 ± 6 in G12.89+0.49, G16.86–2.16, and G28.28–0.36, respectively.

The $^{12}C/^{13}C$ ratios derived from observations (Table 9) are generally lower than or consistent with those calculated from Equation (5) within errors, except for non-detection species. These results mean that the $^{13}C$ species of $^7$H$_3$N are not heavily diluted. The $^{12}C/^{13}C$ ratios of cyanopolyynes in dark clouds (e.g., TMC-1, L1521B, and L134N; Taniguchi et al. 2016a, 2017a) are generally lower than those of other carbon-chain species (e.g., CCH, CCS, C$_2$S, C$_3$H), which means that the $^{13}C$ species of cyanopolyynes are not heavily diluted. Similar results with the $^{12}C/^{13}C$ ratios of $^7$H$_3$N being not significantly high were also found in the warm gas around the protostar L1527 (Taniguchi et al. 2016b). Our results show a similar tendency to local low-mass star-forming regions.

Belloche et al. (2016) reported a tentative detection of DC$_3$N toward the Sgr B2 (N2) hot core and derived the D/H ratio to be 0.09%. A tentative detection of DC$_3$N was also achieved toward the Compact Ridge and the hot core of Orion KL (Esplugues et al. 2013), and the deuterium fractionation was estimated at 1.5% ± 0.9%. The latter in the high-mass protostellar object NGC2264 CMM3 was calculated at 1.8% ± 1.5% from a tentative detection of DC$_3$N (Watanabe et al. 2015). Higher D/H values were reported toward cold dense cores (5%–10%), Howe et al. 1994 and toward the L1527 protostar, which is a WCCC source (~3%, Sakai et al. 2009b). The D/H values of HC$_3$N in G16.86–2.16 and G28.28–0.36 (~1%–5%) are higher than that in Sgr B2, lower than in cold dense cores, and comparable to the Orion KL hot core and L1527. On the other hand, DC$_3$N was not detected in G12.89+0.49 and we only derived an upper limit for its D/H ratio, which is significantly lower than those in G16.86–2.16 and G28.28–0.36. In general, the D/H ratio becomes lower in higher temperature regions (e.g., Caselli & Ceccarelli 2012). Hence, the results imply that the emission of HC$_3$N comes from the G12.89+0.49 central hot core position, and the lukewarm envelope component is less than in the other two sources. In the observations presented here, the lukewarm envelopes and the central cores were covered by the single-dish beam, and we cannot distinguish between them. The D/H ratio significantly depends on the temperature, and we need high spatial resolution observations using interferometers such as ALMA to derive the temperature dependence of the D/H ratio.

5.6. Comparison of the Line Width of CH$_3$OH

Line width is a key tool to characterize environments where molecules exist. In general, high excitation energy lines are expected to trace the hotter gas and show broad line widths, whereas low excitation energy lines come mainly from cold molecular clouds and show narrow line widths. We detected several CH$_3$OH emission lines with different excitation energies. We will investigate the relationship between excitation energy and the line width of CH$_3$OH in this subsection.

Figure 11 shows a comparison between the line widths of CH$_3$OH and the excitation energy of each line. We derive the line width ($\Delta v$) using

$$\Delta v = \sqrt{\Delta v_{\text{obs}}^2 - \Delta v_{\text{inst}}^2},$$  \hspace{1cm} (6)

where $\Delta v_{\text{obs}}$ and $\Delta v_{\text{inst}}$ are the observed line widths (Tables 5 and 7) and the instrumental velocity width (0.85 km s$^{-1}$–0.86 km s$^{-1}$, Section 2), respectively.

We conducted the Kendall’s $\tau$ correlation coefficient test. The probability ($p$) that there is no correlation between the line width and the excitation energy is calculated as 0.03%, and the $\tau$ value is +0.51 in G12.89+0.49. This suggests a weak positive correlation between the line width and the excitation energy. The $p$ and $\tau$ values are derived to be 0.69% and +0.08 in G16.86–2.16, respectively. In G28.28–0.36, the $p$ and $\tau$ values are 72% and −0.45. Hence, there is no clear correlation between the line width and the excitation energy. This may be caused by the non-detection of very high excitation energy lines in these two sources.

We also compared the distributions of the CH$_3$OH line widths among the three sources using the two-sample Kolmogorov–Smirnov test. We compared the distributions for all of the combinations: (a) G12.89+0.49 and G28.28–0.36, (b) G16.86–2.16 and G28.28–0.36, and (c) G12.89+0.49 and G16.86–2.16. The probabilities that the distributions of the line widths in the selected two sources are the same are derived to be 3.2 × 10$^{-4}$%, 5.8 × 10$^{-3}$%, and 39% for cases (a), (b), and (c), respectively. These results mean that the distribution of the CH$_3$OH line width in G28.28–0.36 is clearly different from those in the other two sources, and we cannot exclude the possibility that the distributions in G12.89+0.49 and G16.86–2.16 are identical.

The average line widths of CH$_3$OH are 4.8 ± 0.6, 5.2 ± 0.6, and 2.6 ± 0.5 km s$^{-1}$ in G12.89+0.49, G16.86–2.16, and G28.28–0.36, respectively. Although the average line widths in G12.89+0.49 and G16.86–2.16 are consistent with each other within errors, G16.86–2.16 shows the highest value; nevertheless very high excitation energy lines were not detected in G16.86–2.16. This implies that CH$_3$OH exists in
turbulent gas such as a molecular outflow in G16.86−2.16 rather than hot gas. This is supported by the strong wing emission in the CH$_3$OH spectra in G16.86−2.16. In G12.89+0.49, CH$_3$OH seems to exist in the hot gas as well as in a molecular outflow, as suggested by the wing emission. On the other hand, the line width in G28.28−0.36 is much narrower than those in the other two sources. This suggests that CH$_3$OH for this source exists mainly in the relatively quiescent region, i.e., the envelope. The non-detection of very high excitation energy lines is consistent with the envelope origin. There is the possibility of a molecular outflow origin, but the low S/N prevents us from confirming this.

6. Conclusions

We carried out observations in the 42−46 and 82−103 GHz bands with the Nobeyama 45 m radio telescope, and in the 338.2−339.2 and 348.45−349.45 GHz bands with the ASTE 10 m telescope toward three high-mass star-forming regions associated with the 6.7 GHz CH$_3$OH masers, G12.89+0.49, G16.86−2.16, and G28.28−0.36. The rotational temperatures and the beam-averaged column densities of HC$_3$N, CH$_2$CCH, and CH$_3$OH in the three sources are derived.

The $N$(HC$_3$N)/$N$(CH$_3$OH) ratio in G28.28−0.36 is higher than that in G12.89+0.49 by one order of magnitude and higher than that in G16.86−2.16 by a factor of ~5. Moreover, the relationships between the $N$(HC$_3$N)/$N$(CH$_3$OH) and the $N$(CH$_2$CCH)/$N$(CH$_3$OH) ratios in G28.28−0.36 and G16.86−2.16 are similar to each other, while HC$_3$N is deficient compared to CH$_2$CCH in G12.89+0.49. These results imply chemical diversity of the lukewarm envelope.

The line density in G28.28−0.36 is significantly low and a few COMs have been detected, while oxygen-/nitrogen-bearing COMs and high excitation energy lines have been detected from G12.89+0.49. These results seem to imply that organic-poor MYSOs (G28.28−0.36) are surrounded by a carbon-chain-rich lukewarm envelope, whereas organic-rich MYSOs (G12.89+0.49 and G16.86−2.16; hot cores) are surrounded by a CH$_3$OH-rich lukewarm envelope. The results presented in this paper were based on observations with single-dish telescopes without information about the spatial distributions of each molecular emission and only a few molecular species. Further observations are required to confirm the trends reported in this work.

We thank the anonymous referee who gave us valuable comments which helped us improve the quality of the paper. We would like to express our deep thanks to the members of the Nobeyama Radio Observatory. The Nobeyama Radio Observatory is a branch of the National Astronomical Observatory of Japan (NAOJ), National Institutes of Natural Sciences. The Z45 receiver is supported in part by a Granting-Aid for Science Research of Japan (24244017). We thank to the operation staff members of the ASTE. The ASTE telescope is operated by the NAOJ. K.T. appreciates support from a Granting-Aid for Science Research of Japan (17J03516). L.M. acknowledges support from the NASA postdoctoral program. A portion of this research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

Facilities: Nobeyama 45 m radio telescope, Atacama Submillimeter Telescope Experiment (ASTE).

Software: Java NEWSTAR (https://www.nro.nao.ac.jp/~nro45mrt/html/obs/newstar/).

ORCID iDs

Kotomi Taniguchi @ https://orcid.org/0000-0003-4402-6475
Masao Saito @ https://orcid.org/0000-0003-0769-8627
Liton Majumdar @ https://orcid.org/0000-0001-7031-8039
Tomomi Shimoikura @ https://orcid.org/0000-0002-1054-3004
Kazuhito Dobashi @ https://orcid.org/0000-0001-8058-8577
Fumitaka Nakamura @ https://orcid.org/0000-0001-5431-2294
Tomoya Hirota @ https://orcid.org/0000-0003-1659-095X
Tetsuhiro Minamidani @ https://orcid.org/0000-0001-9778-6692
Yusuke Miyamoto @ https://orcid.org/0000-0002-5560-5168
Hiroyuki Kaneko @ https://orcid.org/0000-0002-2699-4862

References

Aikawa, Y., Wakelman, V., Garrod, R. T., & Herbst, E. 2008, ApJ, 674, 993
Bacmann, A., Taquet, V., Faure, A., Kahane, C., & Ceccarelli, C. 2012, A&A, 541, L12
Balucani, N., Ceccarelli, C., & Taquet, V. 2015, MNRAS, 449, L16
Belloche, A., Müller, H. S. P., Garrod, R. T., & Menten, K. M. 2016, A&A, 587, A91
Bisschop, S. E., Jørgensen, J. K., van Dishoeck, E. F., de Wachter, E. B. M. 2007, A&A, 465, 913
Caselli, P., & Ceccarelli, C. 2012, A&ARv, 20, 56
Cernicharo, J., Marcelino, N., Roueff, E., et al. 2012, ApJL, 759, L43
Halfen, D. T., Woolf, N. J., & Ziurys, L. M. 2017, ApJ, 845, 158
Hasegawa, T. I., & Herbst, E. 1993, MNRAS, 261, 83
Hassell, G. E., Herbst, E., & Garrod, R. T. 2008, ApJ, 681, 1385
He, J. H., Takahashi, S., & Chen, X. 2012, ApJS, 202, 1
Herbst, E., & van Dishoeck, E. F. 2009, ARA&A, 47, 427
Hirota, T., Ohishi, M., & Yamamoto, S. 2009, ApJ, 699, 585
Howe, D. A., Miller, T. J., Schilke, P., & Walmsley, C. M. 1994, MNRAS, 267, 59
Iguchi, S., & Okuda, T. 2008, PASJ, 60, 857
Imai, M., Sakai, N., Oya, Y., et al. 2010, ApJL, 830, L37
Jaber, A. A., Ceccarelli, C., Kahane, C., & Caux, E. 2014, ApJ, 791, 29
Kamazaki, T., Okumura, S. K., Chikada, Y., et al. 2012, PASJ, 64, 29
Lahuis, F., & van Dishoeck, E. F. 2000, A&A, 355, 699
Li, F. C., Xu, Y., Wu, Y. W., et al. 2016, AJ, 152, 92
Majumdar, L., Gratier, P., Andron, I., Wakelam, V., & Caux, E. 2017a, MNRAS, 467, 3525
Majumdar, L., Gratier, P., Ruaud, M., et al. 2017b, MNRAS, 466, 4470
Marcelino, N., Cernicharo, J., Agúndez, M., et al. 2007, ApJL, 665, L127
Michaël, S., Savage, C., Brewster, M. A., Ziurys, L. M., & Wyckoff, S. 2005, ApJ, 634, 1126
Müller, H. S. P., Schlöder, F., Stutzki, J., & Winnewisser, G. 2005, JMS, 742, 215
Nakajima, T., Kimura, K., Nishimura, A., et al. 2013, PASP, 125, 252
Nakamura, F., Ogawa, H., Yonekura, Y., et al. 2015, PASJ, 67, 117
őberg, K. I., Bottinelli, S., Jørgensen, J. K., & van Dishoeck, E. F. 2010, ApJ, 716, 825
Okuda, T., & Iguchi, S. 2008, PASJ, 60, 315
Potapov, A., Sánchez-Monge, A., Schilke, P., et al. 2016, A&A, 594, A117
Purcell, C. R., Balasubramanyam, R., Burton, M. G., et al. 2006, MNRAS, 367, 553
Purcell, C. R., Longmore, S. N., Burton, M. G., et al. 2009, MNRAS, 394, 323
Reboussin, L., Wakelam, V., Guilloteau, S., & Hersant, F. 2014, MNRAS, 440, 3557
Reid, M. J., Menten, K. M., Brunthaler, A., et al. 2014, ApJ, 783, 130
Ruaud, M., Wakelam, V., & Hersant, F. 2016, MNRAS, 459, 3756
Sakai, N., Sakai, T., Hirota, T., Burton, M., & Yamamoto, S. 2009a, ApJ, 697, 769
Sakai, N., Sakai, T., Hirota, T., & Yamamoto, S. 2008, ApJ, 672, 371
Sakai, N., Sakai, T., Hirota, T., & Yamamoto, S. 2009b, ApJ, 702, 1025
Savage, C., Apponi, A. J., Ziurys, L. M., & Wyckoff, S. 2002, ApJ, 578, 211
Shimajiri, Y., Sakai, T., Kitamura, Y., et al. 2015, ApJS, 221, 31
Suzuki, H., Yamamoto, S., Ohishi, M., et al. 1992, ApJ, 392, 551
Taniguchi, K., Ozeki, H., Saito, M., et al. 2016a, ApJ, 817, 147
Taniguchi, K., Ozeki, H., & Saito, M. 2017a, ApJ, 846, 46
Taniguchi, K., Saito, M., Hirota, T., et al. 2017b, ApJ, 844, 68
Taniguchi, K., Saito, M., & Ozeki, H. 2016b, ApJ, 830, 106
Taniguchi, K., Saito, M., Sridharan, T. K., & Minamidani, T. 2018, ApJ, 854, 133
Tielens, A. G. G. M., & Hagen, W. 1982, A&A, 114, 245
Urquhart, J. S., Moore, T. J. T., Schuller, F., et al. 2013, MNRAS, 431, 1752
van Dishoeck, E. F. 2018, in Proc. IAU Symp. 332, Astrochemistry VII: Through the Cosmos from Galaxies to Planets, ed. M. Cunningham, T. Millar, & Y. Aikawa (Cambridge: Cambridge Univ. Press), 3
Vastel, C., Ceccarelli, C., Lefloch, B., & Bachiller, R. 2014, ApJL, 795, L2
Watanabe, Y., Sakai, N., López-Sepulcre, A., et al. 2015, ApJ, 809, 162