SURVEY OBSERVATIONS OF A POSSIBLE GLYCINE PRECURSOR, METHANIMINE (CH₂NH)

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ABSTRACT

We conducted survey observations of a glycine precursor, methanimine, or methylamine (CH₂NH), with the Nobeyama Radio Observatory 45 m telescope and the Sub-Millimeter Radio telescope toward 12 high-mass and two low-mass star-forming regions in order to increase the number of known CH₂NH sources and to better understand the characteristics of CH₂NH sources. As a result of our survey, CH₂NH was detected in eight sources, including four new sources. The estimated fractional abundances were \( \sim 10^{-8} \) in Orion KL and \( 10.47 \pm 0.03 \), while they were \( \sim 10^{-9} \) toward the other sources. Our hydrogen recombination line and past studies suggest that CH₂NH-rich sources have less (this mean not so evolved) evolved H II regions. The lower destruction rates from UV flux from the central star would contribute to the high CH₂NH abundances toward CH₂NH-rich sources. Our gas-grain chemical simulations suggest that CH₂NH is mostly formed in the gas phase by neutral–neutral reactions, rather than being the product of thermal evaporation from dust surfaces.

Key words: astrochemistry – ISM: abundances – ISM: molecules – line: identification – methods: observational

1. INTRODUCTION

It is widely thought that prebiotic chemical evolution from small to large and complex molecules may have resulted in the origin of life. There are two conflicting views regarding how complex organic molecules (COMs) were formed on the early Earth: formation on the planetary surface or exogenous delivery.

Miller (1953) conducted the very famous Miller–Urey experiment. He demonstrated that organic materials can be synthesized from “inorganic materials,” which went against the “common sense” of the time. He synthesized several organic compounds, such as the amino acids glycine and alanine, by discharging a gas mixture of \( \text{H}_2\text{O}, \text{NH}_3, \text{CH}_4, \) and \( \text{H}_2 \), which was thought to be the atmospheric composition of the early Earth. However, recent studies have suggested that the number of synthesized organic molecules would be dramatically lower under the currently suggested CO₂ dominant atmosphere (Ehrenfreund et al. 2002).

In the interstellar medium (ISM), more than 190 molecules ranging from simple linear molecules to COMs have been detected, mainly toward dark clouds, and low-mass and high-mass star-forming regions (by the Cryogenic Dark Material Search⁶). Ehrenfreund et al. (2002) argued that the exogenous delivery of COMs to the early Earth by comets and/or asteroids may have been greater than their terrestrial formation by three orders of magnitude; molecules delivered from the universe might have played a crucial role in early Earth chemistry. If this is the case, understanding the interstellar chemistry will enable us to better understand the first stage of chemical evolution regarding the origin of life: from atoms to very simple prebiotic species.

Among prebiotic species, great attention has been paid to amino acids, essential building blocks of terrestrial life: many surveys were undertaken, without success, to search for the simplest amino acid, glycine (NH₂CH₂COOH), toward Sgr B2 and other high-mass star-forming regions (e.g., Brown et al. 1979; Snyder et al. 1983; Combes et al. 1996, and references therein). Although Kuan et al. (2003) claimed the first detection of glycine in 2003, several follow-up observations were unable to replicate the detection (e.g., Jones et al. 2007). The difficulties faced by past glycine surveys were due to the potential weakness of glycine lines and the low sensitivities of the telescopes used for the surveys. Now, the Atacama Large Millimeter/submillimeter Array (ALMA) is expected to overcome these difficulties associated with glycine surveys. Garrod (2013) used his three-phase chemical model, which simulates a fully coupled gas phase, grain surface, and bulk ice chemistry, and suggested the possibility of detecting glycine using ALMA.

The formation processes of glycine have been studied by many researchers. Theoretical and laboratory studies have demonstrated that glycine is formed on icy grain surfaces from methylamine (CH₃NH₂) and CO₂ under UV irradiation (Holtom et al. 2005). It has been suggested that CH₃NH₂ can be formed from the abundant species CH₄ and NH₃ on icy dust surfaces (Kim & Kaiser 2011). Alternatively, methylamine (CH₃NH) could be related to the formation of CH₂NH₂. Another possible route to form these species is hydrogenation to HCN on the dust surface, as investigated both experimentally and theoretically (Woon 2002; Theule et al. 2011). These issues have also been discussed in detail by Majumdar et al. (2013), where they identified CH₂NH₂ as another possible precursor for glycine formation.

\[
\text{HCN} \xrightarrow{2H} \text{CH}_2\text{NH} \\
\text{CH}_2\text{NH} \xrightarrow{2H} \text{CH}_3\text{NH}_2
\]

Theule et al. (2011) suggested that the hydrogenation process to CH₂NH might be much quicker compared to that of HCN. It has also been suggested that CH₂NH may be formed in gas-
phase reactions among radicals (Turner et al. 1999; Halfen et al. 2013). Halfen et al. (2013) showed that the excitation temperatures of \( \text{CH}_2\text{NH} \) and \( \text{CH}_3\text{NH}_2 \) are different, suggesting different formation paths for \( \text{CH}_2\text{NH} \) and \( \text{CH}_3\text{NH}_2 \). If this is the case, \( \text{CH}_2\text{NH} \) might not be a direct precursor to \( \text{CH}_3\text{NH}_2 \).

\( \text{CH}_2\text{NH} \) is related to another formation path for glycine; if a \( \text{H} \) atom and \( \text{HCN} \) are added to \( \text{CH}_2\text{NH} \) on the grain surface, aminocetonitrile (\( \text{NH}_2\text{CH}_2\text{CN} \)) could be formed (Danger et al. 2011). \( \text{NH}_2\text{CH}_2\text{CN} \) yields glycine via hydrolysis (Peltzer et al. 1984). These formation processes are shown in Figure 1.

Such precursor candidate molecules were reported in the ISM. The first detection of \( \text{CH}_2\text{NH} \) was made toward Sgr B2 (Godfrey et al. 1973). \( \text{CH}_2\text{NH} \) was confirmed toward Sgr B2 by many authors, and in particular, Halfen et al. (2013) reported 27 transitions of \( \text{CH}_2\text{NH} \) toward Sgr B2. Dickens et al. (1997) reported new detections of \( \text{CH}_2\text{NH} \) in three high-mass star-forming regions, W51 e1/e2, Orion KL, and G34.3 +0.2. Recently, Qin et al. (2010) reported the detection of \( \text{CH}_2\text{NH} \) toward G19.61−0.23 through a line survey with the Sub-Millimeter Array. The previous results of \( \text{CH}_2\text{NH} \) surveys are summarized in Table 1. Further \( \text{CH}_2\text{NH} \) was detected toward Sgr B2 (Kaifu et al. 1974) and Orion KL (Fourikis et al. 1974). Isokoski et al. (2013) conducted a line survey toward G31.41+0.3, and reported detection of \( \text{CH}_3\text{NH}_2 \), \( \text{NH}_2\text{CH}_2\text{CN} \) was detected toward Sgr B2 (Belloche et al. 2008).

The investigation of the glycine formation processes described in Figure 1 would be an important step toward understanding how the “seed of life” was formed from ubiquitous species. One of the ways to discuss the formation processes would be to compare actual \( \text{CH}_2\text{NH} \) abundances under various physical conditions with chemical models. However, the small number of \( \text{CH}_2\text{NH} \) sources makes it difficult to discuss the connections between different physical conditions and \( \text{CH}_2\text{NH} \) chemistry. Survey observations of possible glycine precursors will not only help to determine the physical conditions where \( \text{CH}_2\text{NH} \) is abundant, but also to plan promising future glycine surveys with ALMA.

In this paper, we extended the \( \text{CH}_2\text{NH} \) survey conducted by Dickens et al. (1997) toward high-mass and low-mass star-forming regions, and report four new \( \text{CH}_2\text{NH} \) sources. Our new detections of \( \text{CH}_2\text{NH} \) sources enabled us to discuss the connection between \( \text{CH}_2\text{NH} \) chemistry and physical properties. The observational method will be described in Section 2; our results will be described in Section 3; we will compare the evolutionary stages of the \( \text{CH}_2\text{NH} \) sources in Section 4, where we will also discuss the formation path to \( \text{CH}_2\text{NH} \). We will summarize our findings in Section 5.

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**Figure 1.** Assumed formation scenario for glycine. “\( \text{iq} \)” represents the hydrolysis process. References: (A) Kim & Kaiser 2011; (B) Theule et al. 2011 and Woon 2002; (C) Holtom et al. 2005; (D) Peltzer et al. 1984; (E) Danger et al. 2011.

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Table 1

| Source        | Transitions | \( \nu \) (MHz) | Reference |
|---------------|-------------|-----------------|-----------|
| Sagittarius B2 | 211−202     | 172267.113      | (1)       |
| Orion KL      | 111−100     | 225554.692      | (2)       |
|               | 414−313     | 245125.974      | (2)       |
|               | 711−702     | 250161.865      | (2)       |
|               | 608−515     | 251421.379      | (2)       |
| W51 e1/e2     | 111−100     | 225554.692      | (2)       |
|               | 414−313     | 245125.974      | (2)       |
|               | 608−515     | 251421.379      | (2)       |
|               | 423−322     | 255840.423      | (2)       |
| G34.3+0.2     | 414−313     | 245125.974      | (2)       |
| G19.61−0.23   | 311−202     | 340354.315      | (3)       |

**Notes**

* 27 transitions were reported by Halfen et al. (2013) toward Sagittarius B2.

**References.** (1) Halfen et al. 2013, and references therein; (2) Dickens et al. 1997; (3) Qin et al. 2010.

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Table 2

| Transition           | \( \nu \) (MHz) | \( \theta_p \) ("D") | Telescope |
|----------------------|-----------------|----------------------|-----------|
| 414−313              | 105794.062      | 30.6                 | NRO       |
| 111−100              | 225554.609      | 10.8                 | SMT       |
| 414−313              | 245125.866      | 37.3                 | SMT       |
| 423−322              | 255840.311      | 62.2                 | SMT       |

2. OBSERVATIONS

2.1. Observation Procedure

We conducted survey observations of \( \text{CH}_2\text{NH} \) with the 45 m radio telescope of Nobeyama Radio Observatory (NRO), the National Astronomical Observatory of Japan, in 2013 April, May, and December, and the Sub-Millimeter Radio Telescope (SMT), Arizona Radio Observatory, in 2013 October. The observed lines and their parameters are summarized in Table 2. Various species are observed simultaneously in our observations. The observation and analysis of other species will be presented in a separate paper, with comparisons to the chemical modeling in order to discuss the chemistry of glycine formation.

At NRO, we used the TZ receiver (Nakajima et al. 2013) in the dual polarization mode. The 414−313 transition at 105 GHz was observed. The SAM45 spectrometer was used for the backend with a frequency resolution of 122 kHz, corresponding to a velocity resolution of 0.35 km s\(^{-1}\) at 105 GHz. The system temperature ranged from 150 to 300 K. The main beam efficiency (\( \eta_{\text{main}} \)) was 0.31, and the beam size (FWHM) was 16". Observations were performed in the position switching mode. The pointing accuracy was checked by observing nearby SiO masers, and the pointing error was typically 5", but 10" under windy conditions.

With the SMT telescope, the 111−100, 414−313, and 423−322 lines at 225, 245, and 255 GHz regions, respectively, were observed. Their parameters are summarized in Table 2. We used the 1 mm ALMA SBS SIS receiver in the dual polarization mode. The system temperature was between 250 and 400 K. The main beam efficiency was 0.74. The beam sizes (FWHM) were 35" and 40" depending on the observing frequencies. The position switching mode was employed. The
pointing accuracy was checked using Venus, and its accuracy was kept within 10′. We used Forbes filters as the spectrometer with a frequency resolution of 250 kHz, which is equivalent to the velocity resolution of 0.29 km s⁻¹. Since the Forbes filter has 512 channels, the observed frequency range covered 128 MHz at 225 GHz. For the transitions in 245 and 255 GHz, we split the Forbes filter into two 256 channel sets, and two lines were observed simultaneously.

2.2. Source Selection

Theule et al. (2011) suggested that CH₂NH is formed via the hydrogenation process of HCN (HCN → CH₂NH). To select our target sources, we noted that CH₃OH is well known to be formed via hydrogenation process from CO on the grain surface (CO → H₂CO → CH₃OH). If the formation process to CH₃NH is similar to that of CH₂OH, CH₃NH would potentially be rich toward CH₃OH-rich sources. Thus, our sources were selected from “The Revised Version of Class I Methanol Maser Catalog” (Valtts et al., 2012), and from CH₃OH maser sources (Minier & Booth 2002). We also took into account the results of survey observations of COMs toward hot core sources by Ikeda et al. (2001). Hot cores are high-mass star-forming regions traced by high temperature and dense molecular gas, which are sometimes associated with H II regions. Further, we also selected two famous low-mass star-forming regions where complex molecules have been observed. These 14 sources for our survey are summarized in Table 3.

In this table, W₃(H₂O), Orion KL, NGC 6334F, G10.47 +0.03, G19.61–0.23, G31.41+0.3, W51 e1/e2, and DR21 (OH) are molecule-rich sources (Ikeda et al. 2001). G75.78 +0.34 and Cep A were selected from the CH₃OH maser catalogs. The above sources are high-mass star-forming regions.

3. RESULTS

We detected CH₂NH lines toward eight high-mass star-forming regions as shown in Figure 2. Among them, Orion KL, W51 e1/e2, G34.3+0.15, and G19.61–0.23 are known CH₂NH sources from past surveys (Dickens et al. 1997; Qin et al. 2010). However, we report the detection of the 404→313 transition for the first time. Other sources, NGC 6334F, G10.47+0.03, G31.41+0.3, and DR21(OH), are new CH₂NH sources. The observation results are summarized in Table 4.

Figure 2 shows the detected 404→313 line of CH₂NH with the NRO 45 m telescope toward the eight high-mass star-forming regions. The dotted lines correspond to the rest frequency of the 404→313 transition (105.79462 GHz). Two other CH₂NH lines (414→313 and 423→322) were detected with the SMT telescope toward G10.47+0.03 and G31.41+0.3. We note that the 404→313 lines toward G10.47+0.03 and G31.41+0.3 show comparable intensities to that of Orion KL. Figure 3 shows the CH₂NH lines observed toward G10.47+0.03 and G31.41+0.3 with the NRO 45 m telescope and the SMT telescope. In this figure, the vertical solid line corresponds to the systemic radial velocity of each source, shown in Table 3. The differences between radial velocities among the three observed transitions, 404→313, 414→313, and 423→322, are within 0.25 km s⁻¹. On the other hand, we did not detect the 111→000 transition toward G31.41+0.3.

For other sources (Cep A, W3(H₂O), W3(OH), G75.78 +0.34, NGC 2264 MM3 IRS1, NGC 1333 IRAS4B, and IRAS 16293-2422), no CH₂NH transitions were detected. We briefly summarize their properties here. Cep A is a high-mass star-forming region which harbors several radio continuum sources including several H II regions. These complex components are spatially unresolved in our beam. W3(H₂O) is an H₂O maser source with which H II regions are associated. G75.78+0.34 is known to contain at least two ultra-compact H II regions ionized by B0-B0.5 ZAMS stars and possibly hyper-compact H II regions. NGC 2264 MM3 IRS1 is a dense core associated with a small star cluster, where HCOOCH₃ emission was reported (Sakai et al. 2007). NGC 1333 IRAS4B and IRAS 16293-2422 are class 0 low-mass protostars where COMs have

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Table 3

| Source            | α(J2000) h m s | δ(J2000) ° ′ ″ | V_LSR (km s⁻¹) | Distance (kpc) | Masers | Mass High/Low | Detection | Reference        |
|-------------------|---------------|----------------|----------------|----------------|--------|---------------|-----------|------------------|
| W³(H₂O)           | 02 27 04.6    | +61 52 25      | −47            | 2.0            | M      | H             | no        | 1, 6             |
| NGC 1333 IRAS4B   | 03 29 11.99   | +31 13 08.9    | 6.8            | 0.2            | M      | H             | no        | 3, 7             |
| Orion KL          | 05 35 14.5    | −05 22 36.6    | 6              | 0.4            | M      | H             | confirm   | 1, 8             |
| NGC 2264 MMS3     | 06 41 12.3    | +09 29 11.9    | 8              | 0.7            | M      | H             | no        | 4, 9             |
| IRAS 16293-2422   | 16 32 22.63   | −24 28 31.8    | 2.7            | 0.12           | …      | H             | no        | 5, 10            |
| NGC 6334F         | 17 26 42.8    | −36 09 17.0    | −7             | 1.3            | M      | H             | new       | 1, 6             |
| G10.47+0.03       | 18 08 38.13   | −19 51 49.4    | 68             | 8.5            | M      | H             | new       | 1, 6             |
| G19.61–0.23       | 18 27 38.0    | −11 56 42      | 41.9           | 4.0            | M      | H             | confirm   | 1, 11            |
| G31.41+0.3        | 18 47 34.6    | −01 12 43      | 97             | 7.9            | M      | H             | confirm   | 1, 6             |
| G34.3+0.2         | 18 53 18.54   | +01 14 57.0    | 58             | 1.6            | M      | H             | confirm   | 1, 6             |
| W51 e1/e2         | 19 23 43.77   | +14 30 25.9    | 58             | 5.4            | M      | H             | confirm   | 1, 6             |
| G75.78+0.3        | 20 21 44.1    | +37 26 40      | −0.1           | 3.8            | M      | H             | no        | 2, 6             |
| DR21 (OH)         | 20 39 01.1    | +42 22 50.2    | −3             | 1.5            | M      | H             | new       | 1, 6             |
| Cep A             | 22 56 17.9    | +62 01 49      | −10.5          | 0.7            | M      | H             | no        | 2, 6             |

Note. “M” represents the CH₃OH maser sources reported in Minier & Booth (2002). “H” and “L”, respectively, show high-mass and low-mass star-forming regions. In the column of detection, “no,” “confirm,” and “new,” respectively, represent non-detection sources, confirmations of past CH₂NH surveys, and new CH₂NH detections.

References. (1) Ikeda et al. 2001; (2) Minier & Booth 2002; (3) Sakai et al. 2006; (4) Sakai et al. 2007; (5) Cazaux et al. 2003; (6) Reid et al. 2014; (7) Hirota et al. 2008; (8) Menten et al. 2007; (9) Sung et al. 1997; (10) Loinard et al. 2008; (11) Hofner & Churchwell 1996; (12) Churchwell et al. 1990.
been reported. It is known that IRAS 16293-2422 has three components called A1, A2, and B, which are unresolved in our beam. Outflow activities have been confirmed in A2 and B (Loinard et al. 2013). COMs such as methyl formate ($\text{HCOOCH}_3$) and glycolaldehyde ($\text{CH}_2\text{OHCHO}$) were detected toward IRAS 16293-2422 (Jørgensen et al. 2012). NGC 1333 IRAS4B is located 30″ away from IRAS4A, enabling us to separate them with our beam. HCOOCH3 is detected toward NGC 1333 IRAS4B (Sakai et al. 2006).

3.1. Derivation of Abundance

In this subsection we will describe the methodologies used to derive the fractional abundances of CH$_2$NH. In the following discussion, we will show that reliable CH$_2$NH abundances can be obtained when we employ the same source size as that of the continuum emission. If continuum data are not available, we assume a source size of 10″ in the derivation. The estimated CH$_2$NH abundances under compact source sizes, which will be described later in detail, and a source sizes of 10″ are summarized in Tables 5 and 6, respectively.

For sources where more than two transitions are available, we calculated the column densities of CH$_2$NH using the rotation-diagram method described in Turner (1991), and the following equation was employed:

$$\log \frac{3KW}{8\pi^2\hbar S_I^2 \mu gK} = \log \frac{N}{Q_{\text{rot}}} - \frac{E_u \log e}{kT_{\text{rot}}}$$

where $W$ is the integrated intensity, $S$ is the intrinsic line strength, $\mu$ is the permanent electric dipole moment, $g_I$ and $g_K$ are the nuclear spin degeneracy and the $K$-level degeneracy, respectively, $N$ is the column density, $Q_{\text{rot}}$ is the rotational partition function, $E_u$ is the upper level energy, and $T_{\text{rot}}$ is the rotation temperature. $g_I$ and $g_K$ are unity for CH$_2$NH because CH$_2$NH is an asymmetric top with no identical H atoms. The column density and the excitation temperature can be derived by utilizing least-squares fitting. The column density is derived from the interception of a diagram, and its slope will give us the excitation temperature.

In the excitation analysis above, the beam coupling factors are key parameters. We investigated the distribution of the CH$_2$NH $1_{11}$–$0_{00}$ transition at 225.55455 GHz toward Orion KL using the calibrated Science Verification data of ALMA cycle 0 to estimate CH$_2$NH source sizes. The data were imaged with

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Table 4

| Source            | Obs. freq (GHz) | $T_A^*$ (mK) | $V_{\text{LSR}}$ (km s$^{-1}$) | rms (mK) |
|-------------------|-----------------|-------------|-------------------------------|----------|
| DR21(OH)          | 105.79383       | 24          | 5.4                           | −2.4     | 7        |
| G10.47+0.03       | 105.79429       | 99          | 7.7                           | 67.4     | 11       |
| G31.41+0.3        | 105.79404       | 98          | 2.4                           | 97.1     | 24       |
| G34.3+0.2         | 105.79384       | 42          | 9.7                           | 58.6     | 14       |
| NGC 6334F         | 105.79420       | 47          | 1.8                           | −7.4     | 19       |
| Orion KL          | 105.79352       | 108         | 9.3                           | 7.5      | 13       |
| W51 e1/e2         | 105.79406       | 54          | 11.6                          | 57.0     | 15       |
| G19.61–0.23       | 105.79497       | 31          | 8.5                           | 39.3     | 12       |

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Figure 2. Observed CH$_2$NH $4_{00}$–$3_{13}$ transitions toward the detected sources. The vertical lines represent the rest frequency, 105.794062 GHz.
the Common Astronomy Software Applications (CASA) package. These data have the spectral resolution of 488 kHz and the synthesized beam size of \( \sim 2'' \). We selected line-free channels for continuum subtraction in the \((u, v)\) domain using the CASA task uvcontsub. The channel maps of the \( \text{CH}_2\text{NH} \) 111–000 distribution were made using the CASA task CLEAN. We employed the equal weighting of \( uv \), and set the threshold value to stop the CLEAN task at 72 mJy, considering the rms level. After that, we created the integrated intensity map from 225.55348 to 225.55641 GHz, corresponding to the \( V_{\text{LSR}} \) range from 6.5 to 10.4 km s\(^{-1}\).

Our integrated intensity map of Orion KL is shown in Figure 4(a). The region corresponding to the beam of the NRO 45 m telescope in our survey is shown by the black circle. We

Table 5

| Source       | Size (Components) | \( N[\text{H}_2] \) \((10^{12}\text{cm}^{-2})\) | \( T_{\text{ex}} \) (K) | \( N[\text{CH}_2\text{NH}] \) \((10^{16}\text{cm}^{-2})\) | \( X[\text{CH}_2\text{NH}] \) \((10^{-8})\) |
|--------------|------------------|---------------------------------|-----------------|------------------------------|-----------------|
| Orion KL     | 2'' (3)          | 1.4(a)                          | 88(±23)         | 4.6(±0.7)                    | 3.3(±0.5)       |
| G10.47+0.03  | 1''4             | 6.7(b)                          | 84(±57)         | 21(±7.3)                     | 3.1(±1.1)       |
| G31.41+0.3   | 1''7             | 3.5(b)                          | 28(±17)         | 3.1(±3.0)                    | 0.88(±0.85)     |
| W51 e1/e2    | 1''2 (2)         | 4.0(b)                          | 20(±2)          | 1.1(±0.63)                   | 0.28(±0.16)     |
| NGC 6334F    | 3''7             | 1.4(b)                          | [40]            | 0.3(±0.2)                    | 0.24(±0.14)     |
| G19.61−0.23  | 2''5             | 6.7(c)                          | [40]            | 0.94(±0.65)                  | 0.14(±0.10)     |

Note. \( \text{CH}_2\text{NH} \) column densities ”N,” or its upper limits and fractional abundances “X” are shown. The distributions of \( \text{CH}_2\text{NH} \) were assumed to be equal to the dust continuum. Since it is known that Orion KL has three \( \text{CH}_2\text{NH} \) peaks and W51 e1/e2 has two continuum components, beam coupling factors were modified for these sources. Excitation temperatures are fixed at 40 K (shown with square brackets if only one transition was available) and the uncertainty associated with this assumption is assumed to be 50% of its central value, considering the wide range of excitation temperatures derived with the rotation-diagram method.

References. (a) Hirota et al. 2015; (b) Hernández-Hernández et al. 2014; (c) Wu et al. 2009.
found that there are three strong CH$_2$NH peaks in this region, which are unresolved with the synthesized beam of these data ($\sim$2$''$). In Figure 4(b), CH$_2$NH distributions are compared with the 0.8 mm dust continuum emission in Figure 4 of Hirota et al. (2015). We found that the peak positions of CH$_2$NH are in both the Orion Hot Core and Compact Ridge. There is also a weak peak of CH$_2$NH in the northwest clump. Since the distribution of the CH$_2$NH and dust continuum emission look similar to each other, dust continuum emissions could be good indicators to estimate the source sizes of CH$_2$NH. Thus, if dust continuum data were available, we employed the source size of the dust continuum emission for CH$_2$NH to calculate the beam coupling factors. In this case, column densities of molecular hydrogen were estimated from the dust continuum emission to calculate the fractional abundances of CH$_2$NH (Table 5).

For G10.47+0.03 and G31.41+0.3, we created rotation diagrams to derive the column densities using the three transitions that we observed. For Orion KL and W51 e1/e2, we created rotation diagrams by including other CH$_2$NH transitions reported by Dickens et al. (1997). These results are shown in Figure 5. For these four CH$_2$NH sources, we derived excitation temperatures ranging from 20 to 90 K. Since only one transition was observed toward the other sources, we assumed that the excitation temperature is similar to that of HCOOH (40 K) reported by Ikeda et al. (2001) because the dipole moment of HCOOH is close to that of CH$_2$NH. It would be important to know the error associated with the fractional abundances when the excitation temperature is fixed to be 40 K. Considering that the wide range of excitation temperatures was derived from the rotation-diagram method, we assumed that the excitation temperatures can be changed within ±20 K, which can change the column densities by 40%. We note that the optical depths calculated with our method were less than 0.3, even for strong CH$_2$NH transitions. The CH$_2$NH column densities and the fractional abundances derived assuming compact sources are summarized in Table 5.

For sources for which dust continuum emission data are not available (G34.3+0.2, DR21(OH), W3(H2O), G75.78+0.34, and DR21(OH)), we created rotation diagrams by including other CH$_2$NH transitions that we observed. For Orion KL and W51 e1/e2 in Table 5, we also performed calculations assuming 10$^6$ sources in order to understand how fractional abundance can change depending on the source sizes. The results show that the differences of the fractional abundances in the two different source sizes were within a factor of 3. The upper limits of CH$_2$NH are shown for non-detection sources.

References. (a) Ikeda et al. 2001; (b) Peretto et al. 2006; (c) Jørgensen et al. 2002; (d) Ceccarelli et al. 2000; (e) assumed value.

| Source       | N[H$_2$] (10$^{23}$ cm$^{-2}$) | $T_{ex}$ (K) | N[CH$_2$NH] (10$^{15}$ cm$^{-2}$) | X[CH$_2$NH] (10$^{-8}$) | $X_{\text{compact}}$/X$_{\text{obs}}$ |
|--------------|-------------------------------|-------------|--------------------------------|------------------------|--------------------------------------|
| Orion KL     | 1.0(a)                        | 88±23       | 5.5±0.8                         | 5.5±0.8                | 0.6                                  |
| G10.47+0.03  | 1.3(a)                        | 84±57       | 4.7±1.6                         | 3.6±1.3                | 0.9                                  |
| G31.41+0.3   | 1.6(a)                        | 28±17       | 0.88≤0.82                       | 0.53≤0.51              | 1.7                                  |
| NGC 6334F    | 2.0(a)                        | [40]        | 0.3±0.2                         | 0.16±0.12              | 1.1                                  |
| W51 e1/e2    | 3.6(a)                        | 20±2        | 0.32±0.09                       | 0.09±0.03              | 3.1                                  |
| DR21(OH)    | 2.0(a)                        | [40]        | 0.27±0.21                       | 0.14±0.11              | ...                                 |
| W3(H2O)     | 1.0(a)                        | [40]        | <0.7                            | <0.7                   | ...                                  |
| G75.78+0.34  | 1.0(e)                        | [40]        | <0.6                            | <0.6                   | ...                                  |
| Cep A        | 1.0(e)                        | [40]        | <0.5                            | <0.5                   | ...                                  |
| NGC 2264 MMS3 | 5.7(b)                       | [40]        | <0.1                            | <0.02                  | ...                                  |
| NGC 1333 IRAS4B | 3.0(c)                | [40]        | <0.1                            | <0.04                  | ...                                  |
| IRAS 16293-2422 | 0.8(d)             | [40]        | <0.1                            | <0.2                   | ...                                  |

Note. For the sources for which dust continuum data are not available, a source size of 10$^6$ was assumed to derive the fractional abundances from the spatially extended CO observations. Although we have already obtained more reliable fractional abundances toward Orion KL, G10.47+0.03, G31.41+0.3, NGC 6334F, and W51 e1/e2 in Table 5, we also performed calculations assuming 10$^6$ sources in order to understand how fractional abundance can change depending on the source sizes. The results show that the differences of the fractional abundances in the two different source sizes were within a factor of 3. The upper limits of CH$_2$NH are shown for non-detection sources.

Figure 4. (a) The integrated intensity map of the CH$_2$NH 1$_{11}$-0$_{00}$ transition. The velocity range is from 6.5 to 10.4 km s$^{-1}$ and the spatial resolution is 2$''$. The (0, 0) position corresponds to R.A.(J2000) = 05$^h$35$^m$14$^s$.250, decl. (J2000) = −05$^\circ$.222 36$''$.486. Our observing position with the NRO 45 m telescope is shown by the cross. (b) The red contour map of the CH$_2$NH 1$_{11}$-0$_{00}$ transition is overlapped on the dust continuum emission obtained by Hirota et al. (2015). The (0, 0) position is the same as in (a). The red circles in (b) correspond to the continuum sources reported by Hirota et al. (2015). A green triangle represents the position of the infrared source called “Source n.”
Cep A, NGC 2264 MMS3, NGC 1333 IRAS4B, and IRAS 16293-2422) we assumed, based on extended CO data, that CH$_2$NH is spatially extended (a source size of 10” in calculating the fractional abundances. In this case, both CH$_2$NH and molecular hydrogen may be underestimated due to beam dilution. It is important to know how fractional abundances tend to be affected if we employ a source size of 10”. For this purpose, we calculated CH$_2$NH fractional abundances toward Orion KL, G10.47+0.03, G31.41+0.3, NGC 6334F, and W51 e1/e2 assuming source sizes of 10” (top half of Table 6), and the CH$_2$NH fractional abundance ratio of the compact source to the 10” source were investigated. As a result, we found that the differences of the fractional abundances were within a factor of ∼3 (Table 6). Considering that the dependence on the source sizes was small, we employed a compact source size when dust continuum data were available (Table 5), and we used the source size of 10” to derive the CH$_2$NH fractional abundances for the other sources (the bottom half of Table 6).

3.2. CH$_2$NH Abundances

In Tables 5 and 6, we summarize the results of our analysis. Fractional abundances of CH$_2$NH are compared in Figure 6. Our CH$_2$NH fractional abundance is highest in Orion KL. The column density of CH$_2$NH toward Orion KL is 6.0 (±1.8) × 10$^{14}$ cm$^{-2}$ in Dickens et al. (1997), and our value, assuming a beam filling factor of unity, is 1.2 (±0.4) × 10$^{15}$ cm$^{-2}$, which agrees within a factor of 2. In our calculation with a compact source size, the column density and the corresponding fractional abundance are, respectively, 5.5 (±0.8) × 10$^{15}$ cm$^{-2}$ and 3.3 (±0.5) × 10$^{-8}$.

G10.47+0.03 and G31.41+0.3 are CH$_2$NH-rich sources next to Orion KL. In G10.47+0.03, the fractional abundance is 3.1 (±1.1) × 10$^{-8}$. G31.41+0.3 has the fractional abundance of 8.8 (±8.5) × 10$^{-9}$. The large error of the fractional abundance in G31.41+0.3 is due to scattering of the plots in its rotation diagram (Figure 5). Transitions at much higher energy levels will enable us to determine the column densities more accurately.
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The fractional abundances of other sources are, 2.4 \((\pm 1.6) \times 10^{-9}\), 2.8 \((\pm 1.6) \times 10^{-9}\), 2.4 \((\pm 1.7) \times 10^{-9}\), 1.4 \((\pm 1.1) \times 10^{-10}\), and 1.4 \((\pm 1.0) \times 10^{-9}\), in G34.3+0.2, W51 e1/e2, NGC 6334F, DR21 (OH), and G19.61–0.23, respectively. If an extended source size was assumed, our column density toward W51 e1/e2, 6.6 \((\pm 3.6) \times 10^{13} \text{cm}^{-2}\), was close to that reported by Dickens et al. (1997), 8 \((\pm 0.4) \times 10^{13} \text{cm}^{-2}\). From these results, we found that CH2NH abundances range from \(\sim 10^{-9}\) to \(\sim 10^{-8}\).

CH2NH was not detected with sufficient S/N ratios toward the other sources (W3(H2O), G75.78+0.34, Cep A, NGC 2264 MMS3, NGC 1333 IRAS4B, IRAS 16293-2422). We derived upper limits for the column densities of CH2NH for these sources corresponding to three sigma rms noise levels and excitation temperatures of 40 K. We summarize these results in Table 6.

4. DISCUSSION

4.1. Characteristics of CH2NH-rich Sources

As presented in Figure 6, the observed CH2NH abundances are different by a factor of about 20. What characteristics cause such a large difference between CH2NH abundances? In this section, we will discuss three hypotheses to explain the different CH2NH abundances in terms of the distance, kinetic temperatures, and evolutionary phase of sources.

First, we will discuss the possibility that the differences in CH2NH abundances simply originate from the different distances to the sources. In fact, the beam averaged CH2NH column densities would be high for closer sources since they are less affected by beam dilution. However, the differences depending on the source sizes were small when we compared their CH2NH fractional abundances. In Figure 7, we plotted the CH2NH fractional abundances against the distance to the sources. It is difficult to see a correlation between CH2NH fractional abundances and distances in Figure 7. The difference in CH2NH fractional abundances should due to source properties rather than just an effect of beam dilution.

The second possibility is that the different temperatures of CH2NH sources might contribute to CH2NH abundances. Theule et al. (2011) demonstrated that CH2NH can be formed via the hydrogenation process from HCN on the dust surface (Figure 1). If CH2NH is produced on the dust surface, the gas-phase CH2NH abundance would be lower until the source temperature became high enough to sublimate species from the dust surface. Hernández-Hernández et al. (2014) reported rotation temperatures of CH3CN, which is often used as a tracer of the kinetic temperature, toward 17 sources including G10.47+0.03, NGC 6334F,W51 e2, and W3(H2O). The rotation temperatures were 499 K for G10.47+0.03, 408 K for NGC 6334F, 314 K for W51 e2, and 182 K for W3(H2O). It is notable that W3(H2O), where CH2NH was not detected, has a lower temperature than the CH2NH sources. Thus, this scenario could be convincing when the desorption temperature of CH2NH is high (>180 K). One easy way to roughly estimate the desorption temperature is to use the Clausius–Clapeyron equation (2) and the ideal gas law (3),

\[
\log_{10} P = 4.559 \left(1 - \frac{T}{T_B}\right)
\]

\[
P = 8.314 n T
\]

where \(T_B\) is the boiling point under the standard state, \(T\) is the sublimation temperature under the interstellar gas pressure \(P\), and \(n\) is the number density of the species. We have to be cautious as the desorption temperature derived using this method is an approximate value, and it has uncertainty for two reasons. First, the Clausius–Clapeyron equation is applicable for the phase transition between a pure solid or liquid and a gas. However, the actual interstellar molecules would be far from

Figure 6. Histogram of CH2NH fractional abundances. A source size of 10" was assumed for G34.3+0.2 and DR21(OH). For the other sources, compact source sizes were assumed. The error bars represent the uncertainties associated with the derivation of CH2NH abundances (i.e., rms noise and the error associated with the scattering of the rotation diagrams, and assumption of the excitation temperatures).

Figure 7. Plots of the distances to the sources against the CH2NH fractional abundances. The upper limits of X(CH2NH) are shown for sources where CH2NH is not detected.
pure material, and physisorbed on H2O ice. Despite the differences in physical condition, the Clausius–Clapeyron equation is successful in reproducing the commonly accepted sublimation temperature of H2O (from 90 to 100 K) and CO (from 15 to 18 K) in the ISM, assuming a density from 1 × 10^5 to 1 × 10^7 cm^{-3}. Second, since the boiling point for CH2NH has not been measured, we had to use the theoretically predicted value of 215(±15) K from a chemical database.\(^{10}\)

If we use the CH2NH fractional abundance of 3.1 × 10^{-8} (the value observed in G10.47+0.03) and the molecular hydrogen number density of 10^7 cm^{-3}, the CH2NH number density \(n\) is 0.31 cm^{-3}. In our calculation, we assume initial \(T\) values of from 20 to 200 K (=\(T_0\)) and \(P\) is obtained from Equation (2), then, the next desorption temperature, \(T_d\), is obtained with Equation (3). In these iterations between Equations (2) and (3) we are able to determine the final \(T\) value when the difference of successive temperatures becomes within 1 K. As a result, we found that the estimated desorption temperature of 40 K is quite low compared to the gas temperatures of star-forming regions.

We also calculated the desorption temperature in terms of the equilibrium of microscopic accretion and desorption processes, which may better approximate the interstellar situation. The accretion rate \(R_{acc}(i)\) (cm^{-3} s^{-1}) and the desorption timescale \(t_{evap}\) for the species \(i\) are described in Hasegawa et al. (1992) as shown below:

\[
R_{acc}(i) = \sigma_d \langle v(i) \rangle n_{gas}(i)n_d
\]

\[
t_{evap} = \nu_0^{-1} \exp(E_{D}/kT_{dust}),
\]

where \(\nu_0 = (2n_{D}/\pi^{2/3})m\).

\[
\sigma_d(\langle v(i) \rangle, n_{gas}(i), n_{dust}(i), n_d, E_{D}, n_s, m, r_{dust})(i).
\]

The desorption temperature is defined as the temperature that makes \(\sigma_d\) equal. Assuming a grain radius of 1 × 10^{-5} cm^{-1}, the physical cross section of 3.14 × 10^{-20} cm^{-2} is used for \(\sigma_d\). In Ruada et al. (2015), \(E_{D}\) for CH2NH is assumed to be the same as for CH3OH (5530 K). Although the masses of CH3OH and CH2NH are similar, this assumption may overestimate the desorption temperature for CH2NH, since the OH group in CH3OH can strongly interact with H2O molecules in the interstellar ice. Thus, if we use the desorption temperature of CH3OH, we should be able to estimate the upper limit to the desorption temperature for CH2NH.

We used our simulation results from model A, described in the Section 4.2, to estimate the number density of CH2NH (\(n_{gas}\) and \(n_{dust}\)) just before the warm-up of the core. Under the molecular hydrogen number density of 1 × 10^7 cm^{-3}, \(n_{gas}\) (CH2NH) and \(n_{dust}\) (CH2NH) are roughly 1 × 10^{-7} cm^{-3} and 1 × 10^{-4} cm^{-3}. With this gas density, the dust number density \(n_d\) can be estimated to be 1 × 10^7 cm^{-3}, assuming a gas-to-dust ratio of 0.01. Then, the upper limit to the desorption temperature can be calculated to be 160 K, which is comparable to the dust temperature in W3(H2O). Since CH2NH should be sufficiently desorbed even in W3(H2O), we can conclude that temperature differences between hot core sources could not explain our observational results.

The third hypothesis is that the different CH2NH abundances are related to the evolutionary phases of H\(\eta\) regions inside a hot core. In the ISM, it is well known that star formation starts in a cold pre-stellar core. The gas temperature gradually rises when a protostar is formed inside the core, and finally frozen species on the dust are evaporated into the gas phase when the dust temperature becomes high enough. (As we have already mentioned, some of our sources are known to have high gas temperatures.) Following on from that, CH2NH will gradually be photo-dissociated due to the strong UV field in the vicinity of an evolved H\(\eta\) region inside the core. In this case, the CH2NH-rich sources can be explained as less evolved H\(\eta\) regions than the other sources, as shown below.

The hydrogen recombination lines, which originate from H\(\eta\) regions, are good tools to study the evolutionary state of an H\(\eta\) region. In Figure 8 we compare the strength of a recombination line, H54/\beta, between five CH2NH sources. The observed line properties are summarized in Table 7. In G10.47+0.03 and G31.41+0.3, the observed H54/\beta line is very weak or below the 3 sigma level. For Orion KL, it is well known that recombination lines originate from the foreground H\(\eta\) region; Plambeck et al. (2013) reported that recombination lines were not detected inside the hot core of Orion KL. Our results suggest that the top three CH2NH-rich sources possess less evolved H\(\eta\) regions, while the H54/\beta line is prominent toward W51 e1/e2 and NGC 6334F. These sources are considered to have more evolved H\(\eta\) regions, supporting our scenario. We also note that past observational results also agree with this scenario.

Cesaroni et al. (2010) claimed that G10.47+0.03 contains two deeply embedded hyper-compact H\(\eta\) regions in the hot core while no detectable H\(\eta\) region is present in G31.41+0.3. Although it is difficult to make direct comparisons with our observations, Jimenez-Serra et al. (2011) detected H40\(\alpha\), H34\(\alpha\), and H31\(\alpha\) toward Cep A. Cep A may have an evolved H\(\eta\) region inside it and the dissociation process might result in the non-detection of CH2NH. Considering the above, the difference in evolutionary phase is the most plausible reason to explain the different CH2NH abundances.

4.2. Astrochemical Modeling

It is difficult to discuss the actual formation processes of CH2NH from our observations alone. In this section, we present the results of a gas-grain chemical model and discuss the chemistry of CH2NH.

4.2.1. The Nautilus Chemical Model

To simulate the abundance of CH2NH in hot cores, the NAUTILUS gas-grain chemical model (Semenov et al. 2010; Reboussin et al. 2014) has been used along with the similar physical model used in Garrod (2013), where a collapse phase is followed by a static warm-up phase. This chemical model computes the time evolution of species in the gas phase and at the surface of dust grains. The gas-phase chemistry is described by the public network kida.uva.2014 (Wakelam et al. 2015). During collisions with grains, species from the gas phase can be physisorbed on the surfaces. They can then
diffuse, react, and be evaporated through thermal and non-thermal processes. All details of the model can be found in Ruaud et al. (2015). For our simulations, we have assumed that species are initially in the atomic form, except for H2, with abundances from Garrod (2013). The initial abundance is listed in Table 8.

Figure 8. Observed recombination line “H54β” is shown next to the narrow CH3CHO transition. Its calculated frequency is 79.103866 GHz. For the recombination line toward Orion KL, see the last part of Section 4.1.

### Table 7: Observed Parameters of H54β

| Source        | Tb (mK) | Δν (km s⁻¹) | W (mK km s⁻¹) | X[CH3NH] × 10⁻⁸ |
|---------------|---------|-------------|---------------|-----------------|
| Orion KL      | Not detectedᵇ | …           | …             | 3.3 (±0.5)      |
| G10.47+0.3    | <24     | [30]        | <72           | 3.1 (±1.1)      |
| G31.41+0.3    | 131     | 23.6        | 1018          | 0.89 (±0.85)    |
| NGC 6334F     | 383     | 29.7        | 3762          | 0.24 (±0.17)    |
| W51 e1/e2     | 531     | 30.3        | 5306          | 0.28 (±0.16)    |

Notes: Observed recombination line parameters, brightness temperatures Tb (mK), line widths Δν (km s⁻¹), and integrated intensities W (mK km s⁻¹) are shown. The upper limit was calculated for G10.47+0.03, with a 3σ noise level and a line width of 30 km s⁻¹. We also show the fractional abundances of CH3NH from Table 5.  
b Plambeck et al. (2013).
Table 8
Initial Elemental Abundances Compared to Total Hydrogen Atoms

| Element | Abundance | Element | Abundance |
|---------|-----------|---------|-----------|
| H₂      | 0.499     | Na      | 2.0(−8)   |
| H       | 2.0(−3)   | Mg      | 7.0(−9)   |
| He      | 9.00(−2)  | Si      | 8.0(−9)   |
| C       | 1.40(−4)  | P       | 3.0(−9)   |
| N       | 7.50(−5)  | Cl      | 4.00(−9)  |
| O       | 3.2(−4)   | Fe      | 3.0(−9)   |
| S       | 8.0(−8)   | ...     | ...       |

Note. Elemental abundance used in our chemical reaction model. This table is from Garrod (2013).

Table 9
Peak Temperatures and Densities for the Models

| Model | Peak Density (cm⁻³) | Peak Temperature (K) |
|-------|---------------------|----------------------|
| A     | 1 × 10⁷             | 400                  |
| B     | 1 × 10⁶             | 400                  |
| C     | 1 × 10⁶             | 400                  |
| D     | 1 × 10⁷             | 200                  |

Table 10
Dust Surface Reactions Related to CH₂NH

| Reaction                          | Ea (K) |
|----------------------------------|--------|
| N + CH₃ → CH₂NH                  |        |
| NH + CH₃ → CH₂NH                 |        |
| NH₂ + CH → CH₂NH                 |        |
| HCN + H → HCN                   |        |
| H₂CN + H → CH₂NH                 |        |
| HCNH + H → CH₂NH                 |        |
| CH₂NH + H → CH₂NH₂               |        |
| CH₂NH + H → CH₂NH₂               |        |
| CH₂NH₂ + H → CH₂NH₂              |        |

Note. The dust surface reactions related to CH₂NH are shown. Ea represents the value of the activation barrier. Since radical species are so reactive, radical–radical reactions would have no activation barriers. The activation barriers for HCN and CH₂NH were cited from the theoretical study by Woon (2002).

Table 11
Gas-phase Reactions Related to CH₃NH

| Reaction                               | α    | β     | γ     |
|----------------------------------------|------|-------|-------|
| NH + CH₃ → CH₂NH + H                  | 1.3 × 10⁻¹⁰ | 1.7 × 10⁻⁴ | 0     |
| CH + NH₃ → CH₂NH + H                  | 1.52 × 10⁻¹⁰ | −5 × 10⁻² | 0     |
| CH₂NH₂⁺ + e⁻ → CH₂NH + H              | 1.5 × 10⁻⁷   | −5 × 10⁻¹ | 0     |
| CH₂NH₃⁺ + e⁻ → CH₂NH₂ + H + H         | 1.5 × 10⁻⁷   | −5 × 10⁻¹ | 0     |
| CH₂NH₂⁺ + e⁻ → CH₂NH₂ + H             | 1.5 × 10⁻⁷   | −5 × 10⁻¹ | 0     |

Note. α, β, and γ represent the coefficients for the Arrhenius equation.

4.2.2. The Physical Model

The physical conditions used as input to the chemical model are based on the “fast warm-up model” from Garrod (2013). We have run four different models (A, B, C, and D) with different peak densities and/or temperatures as listed in Table 9. The peak temperatures and densities were selected considering the recent observations toward hot cores (e.g., Hernández-Hernández et al. 2014). We will see how CH₂NH formation processes depend on densities through the comparison of models A, B, and C, and on temperatures through the comparison of models A and D. The gas densities (nH₃) were initially set to be 3 × 10⁵ cm⁻³, which gradually increased up to their peak densities along with the free-fall equation during the collapsing phase. While gas temperatures were fixed at 10 K in the collapsing phase, dust temperatures decreased from 16 to 8 K depending on the visual extinction, which was calculated from the gas density of the cloud. Once the peak densities were achieved, we fixed the densities, and the gas and dust temperatures were raised from ~10 K to their peak temperatures in 7 × 10⁵ years.

4.2.3. Gas and Ice Phase Formation of CH₂NH

As a result of our model, CH₂NH is formed both in the gas phase and on the dust grain surface. We summarize the main
chemical reactions that form CH₂NH on the surfaces in Table 10. The dust surface reaction rates are proportional to both the probability of the reaction $\kappa$ and the diffusion rates of reactant species (Hasegawa et al. 1992). $\kappa$ is proportional to $\exp(-E_A/2)$, where $E_A$ represents the value of the activation barrier. The diffusion rates depend on the exponential of the dust temperature. For the activation barriers of the hydrogenation processes of HCN and CH₂NH, theoretically predicted values by Woon (2002) were employed.

The main reactions in the gas phase that form CH₂NH are summarized in Table 11. CH₂NH is formed both by dissociative recombination processes and neutral–neutral reactions. The rate coefficients of gas-phase reactions are given by the Arrhenius equation, using the coefficients $\alpha$, $\beta$, and $\gamma$:

$$k(T) = \alpha (T/300)^3 e^{-\gamma/T},$$

(7)

where $T$ represents the gas temperature. As shown in Table 11, the dissociative recombination processes have larger reaction rates.

### 4.2.4. Modeling Results and Discussion

The simulated gas-phase CH₂NH abundances (relative to the total proton density; hereafter represented by the symbol X) for the four models A, B, C, and D are presented in Figure 9 using different colors. The origin in the X axis corresponds to the time of start the collapse of the gas. We found that the general behavior of X[CH₂NH] along with the cloud evolution does not depend on the model. X[CH₂NH] is almost the same in each model in the collapsing phase ($<1.4 \times 10^6$ years). X[CH₂NH] decreases just before the warm-up phase ($\sim1.4 \times 10^6$ years), since gas-phase species are accreted on the dust surface due to the high gas density and low temperature environment. After the warm-up phase, X[CH₂NH] increases dramatically. It is important to examine the detailed CH₂NH formation process in this phase to understand the dominant formation path. Following this, X[CH₂NH] decreases via gas-phase reactions with ions and/or radicals.

Which chemical processes are the most dominant formation processes for CH₂NH? In Figure 10, we compare X[CH₂NH] and X[CH₃NH₂] in both the gas phase and the dust grain surface using model A. We can easily recognize that the dust surface abundance before the warm-up phase ($\sim1.4 \times 10^6$ years) and the gas-phase abundance of CH₃NH₂ after warm-up are almost the same. CH₃NH₂ would mainly be formed on the dust surface before the birth of a star and evaporate to the gas phase. On the other hand, the dust surface X[CH₂NH] is very low ($<10^{-12}$) compared to the gas-phase X[CH₂NH], since dust surface CH₂NH is efficiently hydrogenated to CH₃NH₂ during the collapsing phase. We also confirmed the same trend in models B, C, and D. Thus, gas-phase reactions would be the dominant formation process to explain gas-phase X[CH₂NH] in the protostellar stage.

To discuss the most dominant gas-phase reactions in Table 11, we compared their formation rates $k_{\text{rate}}(T, t)$
Formation rates are represented by $k_{\text{rate}}(T, t) = k(T) \times n_1(t) \times n_2(t)$, where $k(T)$ is the temperature-dependent rate constant (cm$^3$ s$^{-1}$) calculated with the Arrhenius equation, and $n_1(t)$ and $n_2(t)$ are the number densities (cm$^{-3}$) of reactant species in each time step. In Figure 11(A)–(D), the time-dependent behaviors of $k_{\text{rate}}(T, t)$ are shown for models A, B, C, and D, after the collapsing phase ($t > 1.4 \times 10^6$ years). In these figures, the formation rates of NH + CH$_3$, CH + NH$_3$, CH$_2$NH$_2^+$ + e$^-$, CH$_2$NH$^+$ + e$, and CH$_3$NH$_2^+$ + e$^-$ are compared. As we can see through the comparison of models A and C, formation rates tend to be lower under a low density environment, due to the low number densities of reactant species. The difference between model A and model D originates from the different rate coefficients determined by the gas temperatures. However, we confirmed that NH + CH$_3$ reactions would be the most dominant formation process in all the models.

Finally, we will mention the origin of these radicals. The dust surface abundances of radicals are very low during the collapsing phase, since unstable species are quickly hydrogenated. In Figure 12(A), we show the X(CH$_3$) in the gas phase and on the dust surface with red and blue lines, and the X[NH] in the gas phase and on the dust surface with green and black lines. The dust surface X(CH$_3$) and X[NH] are both nearly $10^{-12}$ before the warm-up phase ($\sim 1.4 \times 10^6$ years). Since X(CH$_3$) and X[NH] in the gas phase are much higher than $10^{-12}$ after the warm-up phase, gas-phase reactions are essential to explain the abundant X[CH$_3$] and X[NH]. In the data set of KIDA, radicals are formed via the destruction of complex species. We show that the gas-phase abundances of some species are related to the formation of CH$_3$ and NH using model A in Figures 12(B) and (C). The CH$_3$ radical originates from the destruction of larger saturated molecules, like CH$_4$, CH$_3$OH, and CH$_3$NH$_2$, by atoms and/or secondary UV radiation (Figure 12(B)). The NH radical is formed via the destruction of NH$_3$ (Figure 12(C)).

We summarize the CH$_2$NH formation process here. During the cold collapsing phase, saturated complex molecules like NH$_3$, CH$_4$, CH$_3$OH, and CH$_3$NH$_2$ are formed on the dust surface. We note that the dust surface CH$_2$NH abundance is quite low in the collapsing phase. During the warm-up phase, these molecules evaporate to a gas, and NH and CH$_3$ radicals are produced through the gas-phase reactions using these evaporated molecules. Finally, newly formed radicals form CH$_2$NH.

### 5. CONCLUSION

The main results of this paper can be summarized as follows:

1. We conducted the survey observations of CH$_2$NH toward high-mass and low-mass star-forming regions; CH$_2$NH were detected in eight high-mass star-forming regions.

![Figure 12](image-url)
Among these, the first detections of CH$_2$NH were made in four objects, G10.47+0.03, G31.41+0.3, DR21(OH), and NGC 6334F. However, CH$_2$NH was not detected toward low-mass star-forming regions.

2. We calculated the column densities and fractional abundances or their upper limits in our sources. The fractional abundances range from ~10$^{-7}$ to ~10$^{-8}$. We also found that Orion KL and G10.47+0.03 have higher CH$_2$NH abundances than the other sources by almost one order of magnitude.

3. The CH$_2$NH-rich sources, Orion KL and G10.47+0.03, have high temperature regions, while their H II regions are less evolved than those of the other sources. CH$_2$NH would be much less likely to be photo-dissociated by UV photons in such an environment.

4. From the results of our chemical model, it appears that CH$_2$NH in the hot sources seems to have formed in the gas phase rather than evaporated from the ices. First, saturated molecules are evaporated from the dust surface during the warm-up phase of the cloud. Second, such species are destroyed in the gas phase to form radicals. Following that, the reactions between CH$_3$ and NH radicals form CH$_2$NH.

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ERRATUM: “SURVEY OBSERVATIONS OF A POSSIBLE GLYCINE PRECURSOR, METHANIMINE (CH$_2$NH)”
(2016, ApJ, 825, 79)

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On page 1 of the published version of this article, the incorrect name for CDMS was used: “the Cryogenic Dark Material Search” should be replaced with “the Cologne Database for Molecular Spectroscopy”.