A multi-transition study of molecules toward NGC 1068 based on high-resolution imaging observations with ALMA

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Abstract

We present 0.8-mm band molecular images and spectra obtained with the Atacama Large Millimeter/submillimeter Array (ALMA) toward one of the nearest galaxies with an active galactic nucleus (AGN), NGC 1068. Distributions of CO isotopic species (13CO and C18O) J = 3–2, CN N = 3–2, and CS J = 7–6 are observed toward the circumnuclear disk (CND) and a part of the starburst ring with an angular resolution of ~1′′3 × 1′′2. The physical properties of these molecules and shock-related molecules, such as HNCO, CH3CN, SO, and CH3OH, detected in the 3-mm band were estimated using rotation diagrams under the assumption of local thermodynamic equilibrium. The rotational temperatures of the CO isotopic species and the shock-related molecules in the CND are, respectively, 14–22 K and upper limits of 20–40 K. Although the column densities of the CO isotopic species in the CND are only from one-fifth to one-third of that in the starburst ring, those of the shock-related molecules are enhanced by a factor of 3–10 in the CND. We also discuss the chemistry of each species, and compare the fractional abundances in the CND and starburst ring with those of Galactic sources such as cold cores, hot cores, and shocked molecular clouds in order to study the overall characteristics. We find that the abundances of shock-related molecules are more similar to abundances in hot cores and/or shocked
clouds than to cold cores. The CND hosts relatively complex molecules, which are often associated with shocked molecular clouds or hot cores. Because a high X-ray flux can dissociate these molecules, they must also reside in regions shielded from X-rays.

Key words: galaxies: individual (NGC 1068) — galaxies: nuclei — ISM: abundances — ISM: molecules — radio lines: galaxies

1 Introduction

It is important to investigate the relationships between the power sources of galaxies [i.e., active galactic nuclei (AGN) and/or starbursts] and the chemical properties of the surrounding dense interstellar medium in order to study the effects on molecular abundances and to probe the power source with molecular line observations. Chemical properties, especially, have been expected to be powerful astrophysical tools for the study of galaxies, because the molecular line observations of different galaxies allow us to study the effects of these different physical properties/activities on the molecular medium. In fact, some groups have suggested that it is possible to diagnose power sources in dust-rich active galaxies using molecular line ratios (e.g., Kohn et al. 2001, 2008; Usero et al. 2004; Krips et al. 2005; Imanishi et al. 2007; Krips et al. 2008; Izumi et al. 2013). For example, elevated HCN emission with respect to CO and/or HCO$^+$ has often been detected toward AGNs (e.g., Kohn et al. 1996, 2003), where it is expected to be the imprint of either strong X-ray irradiation/ionization (e.g., Usero et al. 2004; Krips et al. 2011; García-Burillo et al. 2014) and/or a high-temperature environment caused by AGN activity (e.g., Harada et al. 2010; Izumi et al. 2013). On the other hand, we reported no significant differences in the relative abundances of the carbon-containing molecules C$_2$H and cyclic-C$_3$H$_2$ between one of the nearest galaxies with an AGN, NGC 1068, and the prototypical starburst galaxy, NGC 253. It was concluded that these basic carbon-containing molecules are insensitive to AGNs and/or these molecules exist in a cold gas away from an AGN (Nakajima et al. 2011).

Systematic unbiased scans (i.e., molecular line survey observations) are the most effective method not only for complete understanding of chemical compositions in representational sources, but also for probing the interstellar medium and star formation. Over the last 10 years or so, millimeter/sub-millimeter observing systems with very high sensitivity, wide frequency range, and high velocity resolution have been put to use in a number of telescopes (e.g., Carter et al. 2012; Nakajima et al. 2008, 2013a). With these, we can also obtain higher quality line survey observations of millimeter/sub-millimeter molecular lines toward nearby galaxies as well as Galactic sources. To date, several line surveys have been reported towards the center of NGC 1068 using single-dish telescopes (Snell et al. 2011; Costagliola et al. 2011; Kamenzetzy et al. 2011; Spinoglio et al. 2012; Aladro et al. 2013; Nakajima et al. 2013b). For example, Aladro et al. (2013) compared their results with NGC 253, and they suggested that NGC 1068 has a different chemical composition from those of starburst galaxies. In particular, they determined that the ratios H$^{13}$CN/C$^{34}$S and H$^{13}$CO$^+$/C$^{34}$S are higher in NGC 1068 than in NGC 253. In contrast, the fractional abundances of C$_2$H, CH$_3$OH, HC$_3$N, HCO, and SO show similar values in both types of galaxies. Although the chemical environment of NGC 1068 has become clearer thanks to these line survey observations, contamination from starbursts associated with inner spiral arms/ring (d ~ 30”) could be a problem, if we consider the sizes of the observing beams (15”–70”) in these single-dish telescopes. On the other hand, interferometric imaging of the circumnuclear disk (CND) gives clean measurements of spectral lines, but the observed lines are limited to major species such as $^{12}$CO ($J = 1-0$, 2–1, and 3–2), $^{13}$CO ($J = 1-0$, 2–1, and 3–2), C$^{18}$O ($J = 1-0$ and 2–1), HCN ($J = 1-0$ and 3–2), HCO$^+$ ($J = 1-0$, 3–2, and 4–3), CS ($J = 2–1$), CN (N = 2–1), and SiO ($J = 2–1$) (e.g., Planesas et al. 1991; Kaneko et al. 1992; Jackson et al. 1993; Tacconi et al. 1994, 1997; Helfer & Blitz 1995; Papadopoulos et al. 1996; Schinnerer et al. 2000; Kohn et al. 2008; García-Burillo et al. 2010, 2014; Krips et al. 2011; Tsai et al. 2012) due to the limitation in sensitivity of the existing pre-ALMA (Atacama Large Millimeter/sub-millimeter Array) interferometers. Although it is important to estimate the physical properties, such as temperature and density and so on, only one transition has been observed, except for CO, HCN, and HCO$^+$.

In this situation, we proposed to observe several interesting molecules sensitively with ALMA in the 96–100 and 108–111 GHz (3 mm) regions for lower excitation lines (Takano et al. 2014, hereafter Paper 1) and also 327.5–330.5 and 338.5–342.5 GHz (0.8 mm) regions for higher excitation lines. These frequency regions are rich in molecules, including typical shock/dust-related species and the CO isotopologues. Our aim has been to focus on the effects of strong X-rays and starbursts on the shock and/or dust related molecules, CH$_3$OH, SO, HNCO, and CH$_3$CN, which are well observed in Galactic sources, to study...
chemical and physical conditions. Our observational results with ALMA will be compared with observations in Galactic sources, model calculations, and laboratory experiments to study formation and destruction mechanisms of the above molecules. The complex organic molecules CH$_3$OH and CH$_3$CN are thought to be efficiently produced on dust (e.g., Watanabe & Kouchi 2002; Takano et al. 1995) and subsequently desorbed into gas-phase (Garrod et al. 2008), while HNCO is also thought to be produced at least partially on dust (Quan et al. 2010). The radical SO is thought to have an enhanced abundance in shocked regions (Leen & Graff 1988). However, the abundances and chemical processes forming and destroying these molecules are not well understood in galaxies with active galactic nuclei.

From our observations in the two frequency bands with ALMA, rotational temperatures and column densities can be obtained using intensities of two transitions. The field of view of the 0.8-mm observations is about 18”, which means that only the CND region can be covered with one pointing in NGC 1068. Therefore, we additionally observe a part of the starburst ring at the offset position from the center, so that distributions and abundances of molecules in the starburst environment as well as the CND can be studied. This comparison will enable us to further study the impact of AGNs on the surrounding dense interstellar medium. In Paper 1, we presented the distributions of detected molecules in the 3-mm band, such as $^{13}$CO, C$^{18}$O, $^{13}$CN, CS, SO, HNCO, HC$_3$N, CH$_2$OH, CH$_3$CN, and discussed the implications of diversity. The main results of Paper 1 are that the molecular distributions are reflections of both physical and chemical properties.

In this paper, we report a high-angular-resolution ($\sim 1''$) imaging study of molecular lines in the 0.8-mm band toward NGC 1068 observed with ALMA, and also the calculation of the fractional abundances of shock-/dust-related molecules based on not only the observations in the 0.8-mm band but also the earlier 3-mm band results from Paper 1. Even in its early science operation phase, ALMA was already powerful enough to simultaneously observe four high-excitation molecular lines ($^{13}$CO and C$^{18}$O $J = 3$–2, CN $N = 3$–2, and CS $J = 7$–6) in the 0.8-mm band, uncovering a wide variety of molecular line distributions. We describe our observations and data reduction in section 2, and present the images and spectra of the observed molecular lines and also estimated physical properties of individual molecules in section 3. In section 4, we discuss relationships among the molecular abundances toward the CND and starburst ring in NGC 1068, and Galactic sources such as hot cores, cold cores, and shocked clouds. Throughout the paper, we assume that the distance of NGC 1068 is 14.4 Mpc (Tully 1988; Bland-Hawthorn et al. 1997) at this distance, 1" corresponds to 72 pc.

### Table 1. Observing log.

| Parameter                             | Value                        |
|---------------------------------------|------------------------------|
| Observation date                      | 28 Nov 2011                  |
| Number of antennas                    | 14                           |
| Observing time (min)                  | 71.4                         |
| Bandpass calibrator                   | J0423–013                    |
| Flux calibrator                       | Callisto                     |
| Phase calibrator                      | J0339–017                    |
| Rms noise (mJy beam$^{-1}$)           | (CND/starburst ring)         |
| spw0                                  | 8.6–14.3/9.0–13.6            |
| spw1                                  | 5.4–6.6/5.4–7.6              |
| spw2                                  | 3.2–4.5/3.3–3.7              |
| spw3                                  | 3.5–4.0/3.6–4.5              |
| Synthesized beam$^\dagger$            | (major × minor, P.A.)        |
|                                       | $1.29 \times 1.723, 2.3$    |

$^*$See section 2 for details.

$^\dagger$This parameter is for the spectral window of the lowest frequency (spw0).

### 2 Observations

We observed NGC 1068 using ALMA in Cycle 0 (Early Science program) with band-3 ($\lambda \sim 3$ mm) and band-7 ($\lambda \sim 0.8$ mm) receivers in 2012 January and 2011 November, respectively (ID = 2011.0.00061.S; PI = S. Takano). The details of the 3-mm band observations are described in Paper 1, and the 0.8-mm band observations are explained below. Table 1 summarizes the observational parameters of the 0.8-mm band. The centers of four spectral windows were tuned to 329.50 (spw0), 330.85 (spw1), 340.90 (spw2), and 342.80 (spw3) GHz, each with a 1.875-GHz bandwidth and 3840 channels of 488.28 kHz width. The final results were presented with a velocity resolution of $\sim 20$ km s$^{-1}$ to improve the signal-to-noise ratio. The 14 operational 12-m antennas in the compact array configuration were arranged to span baseline lengths of 20–196 m, which gave a beam size of $1.3 \times 1.2$ ($\sim 90 \times 86$ pc) for the lowest frequency, spw0. A two-pointing mosaic was observed in order to image the CND of $\lesssim 280$ pc ($\lesssim 4''$) in diameter and the surrounding starburst ring of $\sim 2$ kpc ($\sim 30''$) in diameter (Schinnerer et al. 2000). The phase center has been set to $\alpha_{2000.0} = 2^h 42^m 40.798$ and $\delta_{2000.0} = -00^\circ 00' 47'' 3938$ (Schinnerer et al. 2000), which corresponds to the radio position of the active nucleus (Muxlow et al. 1996). The position of a part of the starburst ring is at the offset position from the southwest of the AGN by $(\Delta \alpha, \Delta \delta) = (-10'', -10'')$, where the strongest emission lines of CO and HCN (Schinnerer et al. 2000; Kohno et al. 2008) within the starburst ring are detected. The reason for selecting only two positions in the CND and the starburst ring is that we obtain the difference in physical and chemical properties from comparing these regions in the minimum observation time. The systemic

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**Table 1. Observing log.**

| Parameter                             | Value                        |
|---------------------------------------|------------------------------|
| Observation date                      | 28 Nov 2011                  |
| Number of antennas                    | 14                           |
| Observing time (min)                  | 71.4                         |
| Bandpass calibrator                   | J0423–013                    |
| Flux calibrator                       | Callisto                     |
| Phase calibrator                      | J0339–017                    |
| Rms noise (mJy beam$^{-1}$)           | (CND/starburst ring)         |
| spw0                                  | 8.6–14.3/9.0–13.6            |
| spw1                                  | 5.4–6.6/5.4–7.6              |
| spw2                                  | 3.2–4.5/3.3–3.7              |
| spw3                                  | 3.5–4.0/3.6–4.5              |
| Synthesized beam$^\dagger$            | (major × minor, P.A.)        |
|                                       | $1.29 \times 1.723, 2.3$    |

$^*$See section 2 for details.

$^\dagger$This parameter is for the spectral window of the lowest frequency (spw0).
velocity employed was 1150 km s$^{-1}$, which was taken from Schinnerer et al. (2000). The total integration times on the CND and starburst ring were approximately 30.3 min in each position and the total observation time was 71.4 min. The system noise temperatures including the atmosphere were $\sim$120–250 and $\sim$150–700 K in the upper sideband (USB) and the lower sideband (LSB), respectively, depending on frequency and antennas. Because there is an H$_2$O line due to the atmosphere around 326 GHz, the noise temperatures of the lower frequency region in the LSB (especially spw0) are significantly increased. We obtained the rms noise level of images with channel maps in each spw and position (CND and SW region in the starburst ring), and the values are shown in table 1. The position in each image without molecular line emission was selected for calculation. The rms noises achieved were from 3.2 to 14.3 mJy beam$^{-1}$. The delivered data were already bandpass, flux, and gain (phase and amplitude) calibrated by the ALMA Regional Center. All of the above calibration and imaging were carried out using the Common Astronomy Software Applications (CASA: McMullin et al. 2007). According to the information in CASA, the systematic error of the absolute flux calibration is about 10%–20%.

### 3 Results

#### 3.1 Molecular gas distributions

We have successfully detected C$^{18}$O ($J=3$–2), $^{13}$CO ($J=3$–2), CN ($N=3$–2) and CS ($J=7$–6) in the CND, and the same molecules, except for CS, were also detected in the starburst ring. Figure 1 shows the integrated intensity maps of four clearly detected molecules. These are two-point mosaic images toward the CND and a part of the starburst ring. The C$^{18}$O emission was not significantly detected toward the CND, but is relatively strong in the starburst ring. This feature is similar to the distribution of C$^{18}$O ($J=1$–0) in the 3-mm band observations (Paper 1). On the other hand, $^{13}$CO ($J=3$–2) is very strong in the CND and also detected towards the starburst ring. The CN and CS radicals are very weak and not detected
Fig. 2. Top spectra (a) and (b) are at the central continuum position (in the CND), and the bottom spectra (c) and (d) are at the position of the $^{13}$CO $J=3$–2 intensity peak at the southwest position in the starburst ring (see the caption of figure 1). The primary beam correction and convolution to the beam size of the 3-mm band are applied. The observing frequency is shown as a topocentric value, which is a default reference frame of ALMA. It is necessary to shift the frequency corresponding to $V_{LSR}=1150$ km s$^{-1}$ to obtain the approximate rest frequency.

towards the starburst ring, respectively, but both are clearly detected towards the CND (see also the spectra in figure 2). Moreover, the $^{13}$CO and CN emission features from the CND are spatially separated into two conspicuous knots, and the CS emission is also separated into two knots, albeit faintly.

The difference in the C$^{18}$O and $^{13}$CO distributions as noted in the above paragraph cannot be explained by different excitation conditions, because the abundance ratio of these species is not sensitive to the molecular gas temperature and density. Therefore, this feature is possibly the result of differences in isotopic ratios. The [$^{12}$C]/[C$^{18}$O] isotopic ratios in the Galaxy can be quite diverse. For example, the ratio is 20–25 in the Galactic center clouds (Güsten et al. 1983) and $\sim 89$ in the solar system (Wilson & Matteucci 1992) while in external galaxies, the ratio is also diverse [e.g., $\sim 40$ (Henkel et al. 1993) and $\sim 80$ (Martin et al. 2010) for NGC 253; and $> 100$ for the Clover leaf quasar (Henkel et al. 2010)]. Moreover, the [$^{16}$O]/[C$^{18}$O] isotopic ratios is 250 in the Galactic center clouds (Wilson & Rood 1994), $> 350$ for M 82 (Martin et al. 2010); 145 $\pm$ 36 for NGC 253 (Henkel et al. 2014), $\sim 100$ for Arp 220 (Henkel et al. 2014), and $\geq 177$ for NGC 1068 (Aladro et al. 2013). Given this diversity, differences in the isotopic ratio [$^{12}$C]/[C$^{18}$O] and [$^{16}$O]/[C$^{18}$O] between the CND and the starburst ring of NGC 1068 are possible. Another possibility is the effect of isotope-selective photodissociation, in which the abundance of naturally poor isotopic species are decreased because of their lower optical depth (e.g., Harrison et al. 1995). Details concerning these discussions for NGC 1068 will appear in a separate paper (A. Taniguchi et al. in preparation).

3.2 Line properties in the CND and starburst ring

Figure 2 shows the spectra of all spectral windows toward the CND and starburst ring at the southwest position, which is the $^{13}$CO ($J=3$–2) intensity peak, as mentioned in the caption of figure 2. Tables 2 and 3 list the Gaussian fitted line parameters toward the CND and starburst ring, respectively. The spectra of the LSB consist of spw0 (327.29–330.16 GHz) and spw1 (328.49–330.49 GHz), while those of the USB consist of spw2 (338.68–340.54 GHz) and spw3 (340.56–342.43 GHz). To obtain the spectra and measure the Gaussian fitted line parameters, we convolved all 0.8-mm band images to the beam size of the 3-mm band data ($4\,\prime\prime.21 \times 2\,\prime\prime.36$, P.A. = 176$^\circ$), and then the correction of the primary beam attenuation was applied. $^{13}$CO, CN, and CS were clearly detected toward the CND although C$^{18}$O was not clearly detected ($\sim 4\,\sigma$). On the other hand, C$^{18}$O, $^{13}$CO, and CN were clearly detected toward the starburst ring. Unfortunately, expected emission lines from shock- and/or dust-related molecules, CH$_3$OH, SO, HNCO, and CH$_3$CN, were not detected in the 0.8-mm band. We calculated the upper limits of the integrated flux ($1\,\sigma$) for these molecules from the rms noise level. The line widths are broad in the CND with approximately $170–180$ km s$^{-1}$, except for CN. For CN, two partially separated fine structure components of $J=5/2$–$3/2$ and $J=7/2$–$5/2$ were
identified at the band edge. Therefore the line parameters of CN may not be very precise. Moreover, it is not possible to resolve each hyperfine component. Unlike the case with the CND, the line widths of all detected lines in the starburst ring are narrow, approximately 30–40 km s\(^{-1}\).

### 3.3 Comparison of flux with single-dish telescope

We compared the flux obtained with ALMA with those obtained with the single dish James Clerk Maxwell Telescope (JCMT) to estimate the recovery of the flux with the interferometer. For \(^{13}\)CO \(J = 3–2\), the image obtained with ALMA (primary beam corrected) was convolved with the JCMT beam of 14\(^{\prime}\), and the flux obtained was converted to the brightness temperature, which is 3.4 ± 0.1 K km s\(^{-1}\). The corresponding value obtained with the JCMT is 10.7 ± 1.3 K km s\(^{-1}\), which is observed by Israel (2009). Therefore, the ALMA observations recover 32\% ± 5\% of the single-dish flux. For CS \(J = 7–6\), the flux obtained with ALMA was converted to brightness temperature, which is \(\sim 0.4\) K km s\(^{-1}\). Although the detection of CS \(J = 7–6\) with the JCMT is marginal, the corresponding value is \(\sim 1.4\) K km s\(^{-1}\) (Bayet et al. 2009). Therefore, the recovered flux is about 26\%. The recovered flux of \(^{13}\)CO \(J = 1–0\) in the 3-mm band is about 80\%–90\%, which was obtained by comparing with the single-dish telescopes NRO (Nobeyama Radio Observatory) 45-m and IRAM (Institut de Radioastronomie Millimétrique) 30-m (see subsection 3.4 in Paper 1). The probable reason for the increase in the missing flux in the 0.8-mm band is that the effective minimum baseline of the observations in this band is longer than that for the observations in the 3-mm band. However, the spatially integrated flux over the central 4\(^{\prime}\) region is almost the same as the previous interferometric observation with the SMA (Submillimeter Array; Krips et al. 2011). Krips et al. suggested that the SMA captured most of the emission measured with single-dish observations. Therefore, the missing flux on a more compact scale, especially the CND region, with ALMA will be almost negligible. On the other hand, the impact of the missing flux in the position of the starburst ring will be discussed in sub-subsection 3.4.1.

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**Table 2.** Line parameters in the circumnuclear disk (CND).

| Frequency (GHz) | Molecule | Transition | \(E_u/\text{K}\) | Peak flux (Jy beam\(^{-1}\)) | \(V_{\text{LSR}}\) (km s\(^{-1}\)) | Line width (km s\(^{-1}\)) | Integrated flux (Jy beam\(^{-1}\) km s\(^{-1}\)) |
|----------------|----------|------------|----------------|---------------------------|---------------------------|---------------------------|---------------------------------|
| 329.330546     | \(^{18}\)O | \(J = 3–2\) | 31.76          | 0.02 ± 0.01               | 1106 ± 20                 | 173 ± 47                  | 4.59 ± 1.16                     |
| 329.66437      | HNCO     | \(J_{K_a, K_c} = 15_{0,15}–14_{0, 14}\) | 126.69         | —                         | —                         | —                         | < 0.97 (1 \(\sigma\))         |
| 330.387960     | \(^{13}\)CO | \(J = 3–2\) | 31.64          | 0.13 ± 0.01               | 1102 ± 4                  | 178 ± 9                   | 25.49 ± 1.26                    |
| 331.071548     | CH\(_3\)CN | \(J = 18_{K}–17_{K}\) | 151.09         | —                         | —                         | —                         | < 0.83 (1 \(\sigma\))         |
| 340.031567     | CN\(^{1}\) | \(N = 3–2, J = 5/2–3/2\) | 32.66          | 0.165 ± 0.004             | 1049 ± 8                  | 272 ± 35                  | 47.67 ± 4.38                    |
| 340.247874     | CN\(^{1}\) | \(N = 3–2, J = 7/2–5/2\) | 32.69          | 0.19 ± 0.01               | 1171 ± 7                  | 308 ± 15                  | 62.83 ± 2.52                    |
| 340.714350     | SO        | \(J_N = 7_{8}–6_{7}\) | 81.31          | —                         | —                         | —                         | < 0.76 (1 \(\sigma\))         |
| 342.729781     | CH\(_3\)OH | \(J_{K_a, K_c} = 13_{1,12}–13_{0,13}A^{+}\) | 232.49         | —                         | —                         | —                         | < 0.49 (1 \(\sigma\))         |
| 342.882866     | CS        | \(J = 7–6\) | 65.88          | 0.046 ± 0.004             | 1109 ± 7                  | 183 ± 17                  | 8.88 ± 0.76                     |

\(^{1}\)Rest frequency listed by Lovas (2004) except for HNCO. The rest frequency of HNCO is taken from the Cologne Database for Molecular Spectroscopy (CDMS: Müller et al. 2005). We here list frequencies of \(J_{K_a, K_c} = 15_{0,15}–14_{0, 14}\) for CH\(_3\)CN, \(J = 7/2–5/2\), \(J = 5/2–3/2\) for CN\(^{1}\), and \(F = 9/2–7/2\), \(J = 7/2–5/2\) for CN.

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**Table 3.** Line parameters in the starburst ring.*

| Frequency (GHz) | Molecule | Transition | \(E_u/\text{K}\) | Peak flux (Jy beam\(^{-1}\)) | \(V_{\text{LSR}}\) (km s\(^{-1}\)) | Line width (km s\(^{-1}\)) | Integrated flux (Jy beam\(^{-1}\) km s\(^{-1}\)) |
|----------------|----------|------------|----------------|---------------------------|---------------------------|---------------------------|---------------------------------|
| 329.330546     | \(^{18}\)O | \(J = 3–2\) | 31.76          | 0.20 ± 0.02               | 1216 ± 1                  | 28 ± 3                    | 6.02 ± 0.50                     |
| 329.66437      | HNCO     | \(J_{K_a, K_c} = 15_{0,15}–14_{0, 14}\) | 126.69         | —                         | —                         | —                         | < 0.75 (1 \(\sigma\))         |
| 330.387960     | \(^{13}\)CO | \(J = 3–2\) | 31.64          | 0.53 ± 0.02               | 1216 ± 1                  | 40 ± 2                    | 22.30 ± 0.80                    |
| 331.071548     | CH\(_3\)CN | \(J = 18_{K}–17_{K}\) | 151.09         | —                         | —                         | —                         | < 0.41 (1 \(\sigma\))         |
| 340.031567     | CN\(^{1}\) | \(N = 3–2, J = 5/2–3/2\) | 32.66          | —                         | —                         | —                         | < 0.27 (1 \(\sigma\))         |
| 340.247874     | CN\(^{1}\) | \(N = 3–2, J = 7/2–5/2\) | 32.69          | 0.05 ± 0.01               | 1212 ± 3                  | 42 ± 6                    | 2.41 ± 0.34                     |
| 340.714350     | SO        | \(J_N = 7_{8}–6_{7}\) | 81.31          | —                         | —                         | —                         | < 0.27 (1 \(\sigma\))         |
| 342.729781     | CH\(_3\)OH | \(J_{K_a, K_c} = 13_{1,12}–13_{0,13}A^{+}\) | 232.49         | —                         | —                         | —                         | < 0.31 (1 \(\sigma\))         |
| 342.882866     | CS        | \(J = 7–6\) | 65.88          | —                         | —                         | —                         | < 0.31 (1 \(\sigma\))         |

\(^{*}\)See the footnote of table 2 for details.
3.4 LTE analysis of individual molecules

We constructed the rotation diagrams of observed molecules in the 3-mm band (Paper 1) and the 0.8-mm band (this work) toward each position of the CND and starburst ring (figure 3). All 0.8-mm band images were convolved to the beam size of the 3-mm band data. Thus, the data points of the 3-mm and 0.8-mm bands were obtained from the emission in the same regions. The rotational temperatures ($T_{rot}$) and column densities ($N_{mol}$) are calculated from the slope and intercept at $E_u = 0$ of the diagram under the assumptions that all lines are optically thin, and that a single excitation temperature ($T_{ex}$) characterizes all transitions [the local thermodynamic equilibrium (LTE) assumption] (e.g., Turner 1991). The non-detected lines are plotted with their rms noise level ($3\sigma$), and the upper or lower limits of physical parameters are calculated. For the calculation of $N_{mol}$ for molecules with only one detected transition, we assumed rotational temperatures of $T_{rot} = 5, 10, 15, 30,$ and 45 K. The results of all molecules are shown in tables 4 and 5. The calculated rotation temperatures and column densities of the observed molecules, C$^{18}$O in the starburst ring, CS in the CND, and $^{13}$CO and HC$_3$N in both regions, are listed in table 4. The column densities for the assumed rotation temperatures of C$^{18}$O and CH$_3$CN (CND), HNCO, CN, SO, and CH$_3$OH (CND and starburst ring), and CS (starburst ring) are listed in table 5, because these molecules were detected in only one transition. Note that these rotation diagrams are fitted with only two points, so that the possibility of multiple components at different temperatures cannot be ruled out (Bayet et al. 2009).

3.4.1 C$^{18}$O and $^{13}$CO

The rotation diagrams of C$^{18}$O and $^{13}$CO are shown in figures 3a and 3c, respectively. The C$^{18}$O $J=1$–0 line was not detected toward the CND, thus we obtained a lower limit of $T_{rot} > 14.2$ K. These CO isotopic molecules trace cold gas (8.0 and 8.5 K) in the starburst ring and some warm gas (> 14.2, 21.5 K) in the CND. Aladro et al. (2013) suggested that $^{13}$CO has two different components in the rotation diagram, 4.3 and 24.1 K. In that work, it is possible that the reported emissions from the CND and starburst ring are blended, because they used a single-dish telescope. In addition, they obtained that the $T_{rot}$ of C$^{18}$O is the lowest in all observed molecules, 3.3 K. Therefore, as compared with our result, previous work with the single-dish telescope overestimated the intensity of a vertical axis in the rotation diagram for the purpose of examination of property in the CND. Or, as we saw in subsection 3.3, the flux of the $J = 3$–2 line in the starburst ring with ALMA is not sufficiently recovered.
Fig. 3. Rotation diagrams of molecules in the 3-mm band and the 0.8-mm band with ALMA observations. The results of the 3-mm band are listed in table 2 in Paper 1. The filled circle symbols and solid lines represent results for the CND, and the filled square symbols and dotted lines represent results for the starburst ring.

for this study. If the previous results with the single-dish telescope are accurate enough, the flux in the starburst ring with ALMA should be increased by a factor of 3. Then the $T_{\text{rot}}$ and the column density of $^{13}\text{CO}$ will be 13.4 K and $6.3 \times 10^{16} \text{ cm}^{-2}$, respectively. Although the rotation temperature was increased by about a factor of 1.5, the value of column density was nearly unchanged. We leave the effect of missing flux out of consideration, because these values make only a limited impact on the following discussion.

Unlike other molecules, the column densities of both CO isotopologs in the starburst ring are larger than those in the CND. The column density of $^{13}\text{CO}$ is a factor of 3.5, and that of $^{15}\text{O}$ a factor of 2.4, larger than those in the CND under the assumption of $T_{\text{rot}} = 10$ K. This tendency is the same with $^{12}\text{CO}$. Tsai et al. (2012) calculated the $N_{\text{H}_2}$ in the CND and the starburst ring from the integrated intensity of the $^{12}\text{CO}$ $J = 1-0$ line. $N_{\text{H}_2}$ in the starburst ring in the R15 area, which includes the area of our observations at the southwest region of the starburst ring, is a factor of about 20 larger than those in the CND. On the other hand, although the $^{13}\text{CO}$ $J = 1-0$ line is rather weak and the $^{15}\text{O}$ $J = 1-0$ line is not detected toward the CND (Paper 1), emission of high-$J$ transition lines such as $^{13}\text{CO}$ $J = 3-2$ in our observation and $^{12}\text{CO}$ $J = 6-5$ based on the data by García-Burillo et al. (2014) are strong and clearly detected. Thus, the kinetic temperature in the CND is very high and presumably in a non-LTE environment. In fact, Krips et al. (2011) already obtained that the physical conditions in
the CND are quite warm ($T_{\text{kin}} \geq 200$ K) and dense ($n \approx 10^6$ cm$^{-3}$), as constrained from their observed molecular line ratios based on a large velocity gradient (LVG) analysis. The details of the physical properties based on the LVG analysis of the CO lines obtained from our observations will be described in the other paper (A. Taniguchi et al. in preparation).

### 3.4.2 HNCO and CH$_3$OH

The rotation diagrams of HNCO and CH$_3$OH are shown in figures 3b and 3g, respectively. The HNCO $J_{K_a,K_c} = 15_0-15_{-0}$ and CH$_3$OH $J_{K_a,K_c} = 13_1, 12-13_{0,1}A - +$ lines were not detected toward either the CND or the starburst ring, thus we could obtain only upper limits of $T_{\text{rot}}$. The CH$_3$OH $J_{K} = 2K-1K$ lines are composed of four transitions ($2_{-1}-1_{-2}E, 2_{0}-1_{0}E, 2_{0}-1_{0}A, 2_{1}-1_{1}E$), but the quartet of lines is blended in the spectra from NGC 1068. Therefore, we calculated $T_{\text{rot}}$ using the method for blended lines by Martín et al. (2006). $T_{\text{rot}}$ in the CND and in the starburst ring is less than 28.6 and 36.0 K, respectively, for HNCO, and 40.4 and 38.9 K, respectively, for CH$_3$OH. It is possible that these lines trace warm gas ($\lesssim 30$–40 K). This value of HNCO is consistent with the value of $\sim 30$ K obtained by Aladro et al. (2013). However, they obtained 5.6 K for CH$_3$OH, which is almost six times lower than our result. The column densities of HNCO in the CND are a factor of $\sim 5$ larger than those in the starburst ring, assuming a $T_{\text{rot}}$ of 10–30 K. On the other hand, the column density of CH$_3$OH is not much different between the CND and the starburst ring under the assumption of a similar $T_{\text{rot}}$. If the $T_{\text{rot}}$ in the CND is higher than the starburst ring (e.g., 30 K in the CND and 10 K in the starburst ring), the column density of CH$_3$OH in the CND is a factor of $\sim 3$ larger than that in the starburst ring.

### 3.4.3 CH$_3$CN

The rotation diagram is shown in figure 3d. The $J_{K} = 6_{K}-5_{K}$ line toward the starburst ring and the $J_{K} = 18_{K}-17_{K}$ lines toward both positions are not detected. We obtained an upper limit of $T_{\text{rot}}, < 26.1$ K, in the CND. The column density in the CND ($\sim 1 \times 10^{13}$ cm$^{-2}$) is the smallest among the observed shock-/dust-related molecules. CH$_3$CN is a tracer of star formation in Galactic sources, such as hot cores and outflows from young stellar objects. Therefore, the non-detection of this molecule in the starburst ring, but its detection in the CND, are interesting results. We discuss the abundance of this molecule in sub-subsection 4.2.2.

### 3.4.4 CN

The rotation diagram is shown in figure 3e. We did not observe CN in the 3-mm band, thus we plotted only the $N = 3$–2 transition in the 0.8-mm band. In line survey observations with the NRO 45-m telescope we found that the CN/CO intensity ratios are significantly higher in NGC 1068 ($\sim 2.3$) than in NGC 253 ($\sim 1.1$) and IC 342 ($\sim 0.6$) (Nakajima et al. 2013b). The CN/CO intensity ratios are $\sim 4.3$ in the CND and $\sim 0.1$ in the starburst ring with this ALMA observation. Moreover, the column density of CN in the CND is a factor of 20–50 larger than that in the starburst ring. CN is one of the key molecules to trace X-ray dominated regions (XDRs), as mentioned in theoretical work (e.g., Meijerink et al. 2007). Therefore, the enhancement of intensity and column density of CN in the CND may be the effects of extreme physical conditions such as those that pertain to XDRs.

### 3.4.5 SO

The rotation diagram is shown in figure 3f. The $J_{N} = 7_{N}-6_{N}$ line is not detected toward both the CND and the starburst ring. We obtained upper limits of $T_{\text{rot}}$ in the CND and the starburst ring of 20–26 K. This temperature is consistent with the value of 22.8 K of Aladro et al. (2013). The previous work of SO, with a single-dish telescope, traced mainly the CND, because the distribution of SO is concentrated in the CND and the contribution is less from the starburst ring, as can be seen in figure 2 in Paper 1. The column density in the CND is a factor of 5–6 larger than that in the starburst ring assuming the same $T_{\text{rot}}$. If the rotational temperature in the CND is higher than in the starburst ring, the ratio of column densities changes. For example, if the rotational temperature in the CND is 30 K and that in the starburst ring is 10 K, the column densities will be $2.4 \times 10^{14}$ and $0.2 \times 10^{13}$ cm$^{-2}$, respectively, leading to a column density ratio of approximately 12.

### 3.4.6 CS

The rotation diagram is shown in figure 3h. The $J = 7$–6 line is not detected toward the starburst ring. We obtained an upper limit of $T_{\text{rot}} < 12.1$ K in this region. $T_{\text{rot}}$ in the CND is 13.1 K, which is consistent with the result of 13.9 K found by Bayet et al. (2009). Since the $J = 7$–6 line was only marginally detected by Bayet et al. (2009), they obtained $T_{\text{rot}} = 7.1$ K from a rotation diagram excluding this line. However, our results support the value including the $J = 7$–6 line. Moreover, Bayet et al. (2009) suggested two fitting components, but the CS molecule is distributed not only in the CND, but also in the starburst ring (see figure 1 in Paper 1). Thus, it is possible to have a blending of emission from the starburst ring.

### 3.4.7 HC$_3$N

The rotation diagram is shown in figure 3i. We did not observe HC$_3$N in the 0.8-mm band, and therefore we obtained only the $J = 11$–10 and 12–11 lines in the 3-mm
hand. Using these lines, $T_{\text{rot}}$ in the CND and in the starburst ring is 22.1 and 17.7 K, respectively. These values are not consistent with that of Aladro et al. (2013), where they obtained 7.3 K. The reason for the discrepancy is not clear, but, as can be seen, the value for $J=10–9$ is afield from the fitting line of the values for $J=11–10$ and $12–11$ in their rotation diagram (see figure A.3 of Aladro et al. 2013). Therefore, HC$_3$N has possibly more than one component in the CND. The column density of HC$_3$N in the CND is about an order of magnitude larger than that in the starburst ring.

### Table 6. Individual fluxes of the molecular lines from the two knots in the CND.

| Molecular line | Component | $\Delta \alpha^*$ ($''$) | $\Delta \delta^*$ ($''$) | Integrated flux (Jy beam$^{-1}$ km s$^{-1}$) | Flux ratio (E-knot/W-knot) |
|---------------|-----------|-------------------------|-------------------------|---------------------------------|--------------------------|
| $^{13}$CO ($J=3–2$) | E-knot | +0.7 | 0.0 | 16.8 ± 0.6 | 0.6 | 1.8 |
| | W-knot | −1.8 | +0.5 | 7.7 ± 0.7 | 2.2 ± 0.2 |
| CN ($N=3–2$) | E-knot | +0.6 | −0.1 | 59.8 ± 3.3 | |
| | W-knot | −1.7 | +0.8 | 26.2 ± 3.8 | |
| CS ($J=7–6$) | E-knot | +0.6 | −0.2 | 7.3 ± 0.5 | |
| | W-knot | −1.8 | +0.4 | 2.1 ± 0.4 | 3.5 ± 0.7 |

*The offset from the central radio continuum position ($\alpha_{2000}=05^h42^m40^s70912$ and $\delta_{2000}=−00^\circ00'47''938$: Gallimore et al. 2004).

4 Discussion

4.1 Knot components in the CND

The asymmetrical distributions of $^{13}$CO, CN and CS in the CND can be seen in figure 1. Usero et al. (2004) suggested that two velocity components, which are “velocity < systemic velocity” and “velocity > systemic velocity,” correspond to the eastern knot (E-knot) and the western knot (W-knot), respectively, in the spectra of CO, CS, HCN, SiO, H$_3^{13}$CO$^+$, HCO$^+$, and HOC$^+$. The E-knot and W-knot are clearly separated in the integrated intensity maps of $^{13}$CO, CN, and CS (figure 1) in our observations. So far, $^{12}$CO $J=1–0$ and 2–1 (Schinnerer et al. 2000), CN $N=2–1$ (García-Burillo et al. 2010), HCN $J=3–2$, HCO$^+$ $J=3–2$, and $^{13}$CO $J=1–0$, and 2–1 (Krips et al. 2011) have been found to be associated with both the E-knot and the W-knot with high-resolution interferometric observations. We find similar distributions for $^{13}$CO ($J=3–2$), CN ($N=3–2$), and CS ($J=7–6$) for the first time with our ALMA observations.

We have measured the peak positions for the E-knot and W-knot seen in these lines, as well as the flux ratios of the E-knot/W-knot for each molecule, both of which are listed in table 6. All measured peak positions of the E-knot and W-knot seen in these molecules are consistent with each other. The flux ratios between the E-knot and W-knot are 2.2 ± 0.2 for $^{13}$CO, 2.3 ± 0.4 for CN and 3.5±0.7 for CS; i.e., the E-knot/W-knot flux ratio of CS is higher than those of $^{13}$CO and CN. Krips et al. (2011) obtained the E-knot/W-knot flux ratios of $^{12}$CO ($J=1–0$, 2–1, and 3–2), $^{13}$CO ($J=1–0$ and 2–1), HCN ($J=3–2$), and HCO$^+$ ($J=3–2$) to be 1.0–2.3 with SMA and PdBI (Plateau de Bure Interferometer) observations, and Usero et al. (2004) shows the ratios of $^{12}$CO ($J=1–0$ and 2–1), HCN ($J=1–0$), SiO ($J=2–1$ and 3–2), H$_3^{13}$CO$^+$ ($J=1–0$), HCO$^+$ ($J=1–0$), and HOC$^+$ ($J=1–0$) with IRAM 30-m observations to be 0.6–1.8 and CS ($J=2–1$) to be 2.2. Therefore, the measured E-knot/W-knot flux ratio of CS ($J=7–6$) is higher than that of any of the other molecular lines. These results suggest that there is a chemical differentiation between the E and W knots in the CND (e.g., Usero et al. 2004). However, the details of the chemical differentiation and/or the physical structure in the CND are still not clear based on our observations with the spatial resolution available with ALMA during Cycle 0.

4.2 Fractional abundances

In order to understand which mechanism, such as X-rays, shock waves, or ultraviolet photons, dominates the observed chemical features, it is helpful to obtain fractional abundances of each species with respect to molecular hydrogen. There are several different possible driving forces of chemistry in the observed regions of NGC 1068. For example, since the AGN emits intense X-rays, it is likely to have XDRs (e.g., García-Burillo et al. 2010). Elevated massive star formation can create photon-dominated regions (PDRs: e.g., Hollenbach & Tielens 1999) due to ultraviolet radiation from OB stars. In the site of embedded on-going star formation, hot cores can also contribute to molecular emission. Furthermore, the shock waves affect the chemistry by heating up the gas as well as by sputtering dust grains. With our beam size (∼90 pc), a mixture of molecular clouds governed by these different mechanisms may be observed. Less dense gas than the mean density of the molecular cloud is likely to have a higher volume-filling factor,
while emission from compact sources such as hot cores tends to have much smaller volume-filling factors unless the region hosts an extremely large number of hot cores. With this complexity in mind, we derived the fractional abundances and compared our results with various types of Galactic sources to understand the nature of molecular material in the CND and starburst ring in NGC 1068.

To compute fractional abundances, we first need to estimate the column density of molecular hydrogen $N_{\text{H}_2}$, which is often derived from observations of CO molecules. Here we adopt $N_{\text{H}_2}$ values of $7.4 \times 10^{21}$ cm$^{-2}$ at the CND and $2.6 \times 10^{22}$ cm$^{-2}$ at the starburst ring, based on the estimated column densities of $^{13}$CO, which is an optically thin tracer of molecular gas mass. We computed these by the rotation diagram analysis of our ALMA data (summarized in table 4) with an assumption of a [^{13}CO]/[H$_2$] fractional abundance of $2 \times 10^{-6}$ (Dickman 1978). These values can be compared with $N_{\text{H}_2}$ values based on $^{12}$CO line measurements adopting a CO-to-H$_2$ conversion factor ($X_{\text{CO}}$) factor to check the consistency with previous studies. This approach was taken by Tsai et al. (2012), who derived $N_{\text{H}_2}$ values of $5.6 \times 10^{21}$ cm$^{-2}$ at the CND and $1.1 \times 10^{23}$ cm$^{-2}$ at the starburst ring, where a similar angular resolution CO $J = 1-0$ image (produced from visibilities with similar minimum $uv$ distances to our 0.8-mm band data) is available.

We find that the $N_{\text{H}_2}$ values at the CND agree well with each other, whereas we find a factor of ~4 disagreement in the starburst ring between the $N_{\text{H}_2}$ values from Tsai et al. (2012) and our $^{13}$CO multi-transition analysis. This disagreement in the starburst region may be caused by uncertainties in the adopted $X_{\text{CO}}$ factors (see Bolatto et al. 2013 for a recent review on this issue) and/or in the [^{13}CO]/[H$_2$] fractional abundance. Therefore, we should bear in mind that the estimated fractional abundances in each molecule may suffer from uncertainties in the $N_{\text{H}_2}$ values by a factor of a few at least at the starburst ring.

Table 7 lists the derived fractional abundances of molecules in the CND and starburst ring of NGC 1068. Large differences in the fractional abundances are derived between the two sources for HNCO, CH$_3$CN, CN, SO, CH$_3$OH, CS, and HC$_3$N. There are a number of possible reasons for this difference. First, because the CND is denser than the starburst ring, species with higher critical densities may have higher emission in the CND, as discussed in Paper 1. Also, in the starburst ring, relatively more complex molecules such as HNCO, CH$_3$CN, CH$_3$OH, and HC$_3$N can be more easily photo-dissociated because of the lower density. For granular species, lower abundances in the starburst ring can also result from relatively fewer shocked clouds or hot cores compared with the CND, where molecular clouds are heated up so that desorption can occur efficiently, either by gravitational contraction leading to a hot core or by shock waves. Finally, the large uncertainties in the H$_2$ column densities can lead to large error bars in the fractional abundances with respect to H$_2$. Below we discuss the chemistry of each species, and compare the observed abundances in the CND and starburst ring with those of Galactic sources such as TMC-1 (cold core), Sgr B2(N), and AFGL 2591 (hot cores), and L1157 (B1) (shocked molecular cloud). Comparisons are mostly done for the CND, because the lower fractional abundances of molecules in the starburst ring can be caused by any reason stated above.

**Table 7.** Estimated fractional abundances of molecules in the CND and starburst ring of NGC 1068 along with various Galactic sources as references.

| Species | CND [NGC 1068] | Starburst ring [NGC 1068] | Cold core [TMC-1] | Hot cores [Sgr B2(N)] | Hot cores [AFGL 2591] | Shocked cloud [L1157(B1)] |
|---------|----------------|---------------------------|------------------|---------------------|----------------------|--------------------------|
| HNCO    | $0.7^{+1.0}_{-0.1}(-8)$ | $0.4^{+1.2}_{-0.2}(-9)$ | $5.7 \pm 0.4(-10)$ | $5.6(-10)$ (halo)$^\dagger$ | $1.2(-8)$ (core)$^\ddagger$ | $1.1 \pm 0.7(-8)^{\dagger\dagger}$ |
| CH$_3$CN | $1.1^{+1.6}_{-0.1}(-9)$ | — | $6(-10)^{\dagger}$ | $2.2(-7)$ (core)$^\ddagger$ | $7.0 \pm 0.7(-12)^{\ddagger\ddagger}$ | $0.7 \pm 0.4(-9)^{\dagger\dagger}$ |
| CN      | $0.5^{+0.1}_{-0.1}(-7)$ | $0.2^{+0.2}_{-0.1}(-9)$ | $5(-9)^{\dagger}$ | $2(-8)$ (halo)$^\ddagger$ | $1(-8)^{\dagger}$ | $2.5(-7)^{\ddagger\ddagger}$ |
| SO      | $1.6^{+0.1}_{-0.1}(-8)$ | $7.7 \pm 0.0(-10)$ | $2(-9)^{\dagger}$ | $3.4(-9)$ (halo)$^\ddagger$ | $\leq 2(-8)^{\dagger}$ | $1.2 \pm 3.4(-5)^{\ddagger\ddagger}$ |
| CH$_3$OH | $3.4^{+0.2}_{-0.1}(-8)$ | $7.3^{+1.1}_{-0.9}(-4)$ | $3(-9)^{\dagger}$ | $1.7(-6)$ (core)$^\ddagger$ | — | $1.9(-7)^{\ddagger\ddagger}$ |
| CS      | $3.7^{+0.1}_{-0.1}(-8)$ | $1.5^{+0.4}_{-0.1}(-9)$ | $4(-9)^{\dagger}$ | $2(-8)^{\dagger}$ | $5(-9)$ (halo)$^\ddagger$ | $1.0(-8)^{\ddagger\ddagger}$ |
| HC$_3$N | $1.2(-8)$ | $3.8(-10)$ | $2(-8)^{\dagger}$ | $5(-9)^{\dagger}$ | $7(-9)^{\dagger}$ | $1(-7)^{\dagger}$ |

$^\dagger$ The expression $a(-b)$ represents $a \times 10^{-b}$. In order to obtain the fractional abundances in the CND and the starburst ring, we assume $T_{\text{mb}}$ of $10 \pm 5$ K except for CS in the CND and HC$_3$N, and adopt $N_{\text{H}_2}$ values of $7.4 \times 10^{21}$ cm$^{-2}$ at the CND and $2.6 \times 10^{22}$ cm$^{-2}$ at the starburst ring taken from our $^{13}$CO column densities (see subsection 4.2). References: $^\dagger$ Marcelino et al. (2009), and $N_{\text{H}_2}$ adopted is $1.0 \times 10^{23}$ cm$^{-2}$ (Irvine et al. 1991); $^\ddagger$ Smith, Herbst, and Chang (2004); $^\ddagger\ddagger$ Garrod, Weaver, and Herbst (2008); $^\dagger\dagger$ Nummelin et al. (2000); $^\ddagger\ddagger$ de Vicente et al. (2000); $^\dagger\dagger\dagger$ Minh and Yang (2008), and $N_{\text{H}_2}$ adopted is $2.0 \times 10^{23}$ cm$^{-2}$ (Jiménez-Serra et al. 2012); $^\dagger\dagger\dagger$ Jiménez-Serra et al. (2012); $^\dagger\dagger$ Rodriguez-Fernández et al. (2010); $^\dagger\ddagger$ Arce et al. (2008); $^\ddagger\ddagger$ Bachiller and Perez Gutierrez (1997).
4.2.1 HNCO
Quan et al. (2010) show that HNCO can be formed both in the gas phase and on grain surfaces from OCN either through the gas-phase hydrogenation of protonated species or hydrogenation on grains with neutral atomic hydrogen. In cold or lukewarm cores, gas-phase reactions can produce HNCO with fractional abundances with respect to total hydrogen density of about $10^{-10}$, whereas the abundance can rise to $10^{-8}$ when HNCO on the grain surface sublimates in a hot core or its warm envelope. Shock waves are also likely to cause sublimation of HNCO into the gas-phase, and raise the fractional abundance of gaseous HNCO. The average fractional abundance of HNCO in the CND is comparable to that of a hot core or shocked region (table 7), so that sublimation during warm-up or via shock waves in the CND may be causing the high abundance of HNCO there.

4.2.2 CH$_3$CN
The peak emission of CH$_3$CN in Paper 1 shows no obvious offset from the central radio continuum position as far as we could tell from the current angular resolution of the map. The formation of CH$_3$CN occurs at lower temperatures through a radiative association reaction in the gas-phase (Huntress & Mitchell 1979; Leung et al. 1984)

$$\text{CH}_3^+ + \text{HCN} \rightarrow \text{CH}_3\text{CNH}^+ \quad (1)$$

followed by

$$\text{CH}_3\text{CNH}^+ + e^- \rightarrow \text{CH}_3\text{CN} + \text{H}. \quad (2)$$

As the prestellar core condenses isothermally, CH$_3$CN can freeze on to the dust grains. Additional formation routes of CH$_3$CN are through surface reactions on dust grains. One of them is a series of hydrogenation reactions starting from C$_2$N:

$$\text{C}_2\text{N}(s) + \text{H}(s) \rightarrow \text{HCCN}(s) \quad (3)$$

$$\text{HCCN}(s) + \text{H}(s) \rightarrow \text{CH}_2\text{CN}(s) \quad (4)$$

$$\text{CH}_2\text{CN}(s) + \text{H}(s) \rightarrow \text{CH}_3\text{CN}(s), \quad (5)$$

where (s) stands for solid phase. Another surface reaction to form CH$_3$CN is

$$\text{CH}_3(s) + \text{CN} \rightarrow \text{CH}_3\text{CN}(s), \quad (6)$$

although the route via reactions (3)–(5) is much more efficient in the estimate of the gas-grain model based on the reaction network by Garrod, Weaver, and Herbst (2008), with some added reactions from Harada, Herbst, and Wakelam (2010). CH$_3$CN formed through the above-mentioned routes can again desorb into the gas-phase when a protostar is formed and the collapsing gas and dust heats up, forming a hot core. CH$_3$CN is observed with high abundances in hot cores, especially in regions with higher rotational temperatures (Nummelin et al. 2000). Although the overall abundance in the CND is only slightly higher than that of a cold core and equivalent to that of the shocked cloud, the fractional abundance of CH$_3$CN at its peak location might be much higher. Strong emission of CH$_3$CN near the galactic nucleus in the CND might be coming from star-formation regions.

4.2.3 CN
The distribution of CN emission seems to be clearly separated into the E- and W-knots. CN is an unstable radical, and both chemical models and observations suggest that the CN fractional abundance is high when the chemistry is at an early stage of evolution of molecular clouds or when there is high flux of UV photons, X-rays, and/or cosmic rays to ionize and dissociate precursor molecules such as HCN. Therefore, its fractional abundance in diffuse clouds is high ($\sim 10^{-6}$, in a model by Le Petit et al. 2006), but its fractional abundance decreases as the chemistry evolves to a dense cloud and to hot core/corino. Especially in hot cores, a high-temperature reaction CN + H$_2$ $\rightarrow$ HCN + H efficiently converts CN into HCN (Harada et al. 2010). Although this reaction can reduce the fractional abundance of CN at an elevated temperature caused by shock waves, a young shock still has a high fractional abundance of CN (Mitchell & Deveau 1983). Even in dense regions, the CN fractional abundance can be abundant in PDRs (Jansen et al. 1995) or XDRs with a fractional abundance of $\sim 10^{-7}$ (Meijerink et al. 2007; Harada et al. 2013). The value derived in the CND is closer to the value in XDRs and in the shocked region L1157(B1), but higher than that of cold cores or, especially, hot cores. Since a high X-ray luminosity from the AGN is seen, the high abundance of CN seen in the CND can be explained by XDRs. Although the emissions of CN peak away from AGNs, a model by Harada, Thompson, and Herbst (2013) shows that XDRs can exist in relatively less dense regions $\sim 100$ pc away from the AGN depending on the density structure of the disk. Another possible scenario could be a mixing of ionized/atomic gas with molecular gas caused by turbulence, which is expected to increase the amount of radicals. However, this scenario should be tested by a model.

4.2.4 CH$_3$OH
As mentioned earlier, the emission of CH$_3$OH is separated into the E-knot and W-knot with weaker emission near the AGN core. The most efficient production mechanism
of CH$_3$OH is through grain-surface reactions. A series of hydrogenations starting with CO can occur while the dust is cold ($T \sim 10$ K). In order for methanol to be observed in the gas-phase, methanol on grains must sublime into the gas-phase. In the cold cores, a small amount of methanol can escape into the gas-phase through non-thermal desorption to make a fractional abundance of about $10^{-9}$ (Vasyunin & Herbst 2013). When the dust grains are heated due to either warm-up of the hot core (Garrod et al. 2008) or shock waves (Viti et al. 2011), most of the methanol on grains can sublime into the gas-phase to give a fractional abundance of $\gtrsim 10^{-7}$. The regions that have low abundances of gaseous CH$_3$OH may be free of a mechanism to heat up the dust grains, or the dust can be initially warm so that CO, the precursor species of methanol, desorbs into the gas-phase before it can lead to the formation of methanol. Our observed abundance of CH$_3$OH in the CND is higher than that of cold cores, which suggests that the emission is likely, once again, to be coming from either hot cores or shocked regions. A high abundance of methanol can lead via photolysis and surface chemistry to more complex organic species such as methyl formate (HCOOCH$_3$) and dimethyl ether (CH$_3$OCH$_3$) (Garrod et al. 2008).

4.2.5 HC$_3$N
The emission of HC$_3$N comes from a compact area near the AGN core (Paper 1), probably corresponding to the E-knot. HC$_3$N can be synthesized in the gas-phase, and the peak fractional abundance in cold cores is $2 \times 10^{-8}$, a small factor of 1.7 higher than in the CND. The fractional abundance can increase with an elevation of temperature (Harada et al. 2010, 2013), but too high a value for the X-ray ionization rate can dissociate HC$_3$N, which is therefore not abundant in XDRs. The emission of HC$_3$N in the CND must be coming from regions shielded from X-rays. Since the peak of HC$_3$N, which may be compact, does not seem to be resolved, the fractional abundance of HC$_3$N can only be precisely determined by higher angular resolution data. Therefore, its emission may be coming from hot cores in compact star-forming regions, or more cold and yet dense cores ($n \sim 10^4$ cm$^{-3}$) in a more spread-out distribution. The existence of HC$_3$N suggests that other carbon-chain molecules might also be observable.

4.2.6 CS and SO
The model for the CND by Harada, Thompson, and Herbst (2013) shows that the CS/SO ratio increases with decreasing density both at the free-fall time of a molecular cloud and at steady-state. For both CS and SO, the values in the shocked cloud are more than an order of magnitude higher than those in the cold core. Considering the uncertainty, it is not possible to identify the source of the emission in NGC 1068 by a comparison with these galactic sources. High abundances of the sulfur-containing species SO and CS may result from high elemental sulfur abundance in the gas phase due to shock waves (Wakelam et al. 2005).

4.2.7 Interpretation of chemical features
Overall, the CND hosts relatively complex molecules, which are often associated with shocked molecular clouds or hot cores. Because a high X-ray flux can dissociate these molecules, they must also reside in regions shielded from X-rays.

Although we have derived the column densities of these molecules, there are some difficulties in discerning which exact source the emission is coming from. It is hard to determine whether the CH$_3$CN or HC$_3$N emission is coming from an extended volume of molecular clouds with $n \sim 10^4$ cm$^{-3}$ with a low fractional abundance or from hot cores of $n \sim 10^6$ cm$^{-3}$ and $T \sim 300$ K with a small volume filling factor.

Besides the difference in the density, the difference in abundances of each type of source may also explain the observed emission. For example, low abundances of CH$_3$CN and HC$_3$N are seen in shocked clouds, and their abundances are high in hot cores, so that the differences between the peak locations of CH$_3$OH and HNCO and those of CH$_3$CN and HC$_3$N may come from different environments; viz., hot cores versus shocked clouds. These differences indicate a higher level of star-formation activity within tens of parsecs from the AGN core, where CH$_3$CN and HC$_3$N have peak abundances, albeit considerably lower than expected from hot core material.

It should be also noted that the shock chemistry might also be different around the AGN. The shocked molecular cloud value used in table 7 is from an outflow of the young stellar object L1157. Larger scale shocks in the CND of NGC 1068 may be different in both the pre-shock density and evolutionary timescale of the chemistry.

5 Conclusions
We observed the Seyfert 2 galaxy NGC 1068 with the 0.8-mm band in the CND and starburst ring during the ALMA early science program. The analyses were carried out with our data obtained at the 3-mm band (Paper 1). The main results of this work are summarized in the following list.

(i) We successfully observed images of $^{13}$CO ($J = 3-2$), C$^{18}$O ($J = 3-2$), CN ($N \approx 3-2$), and CS ($J = 7-6$) with an angular resolution of $\sim 1\arcsec.3 \times 1\arcsec.2$. $^{13}$CO and CN
were detected in both the CND and the starburst ring, while CS was only detected in the CND. C\textsuperscript{18}O was not significantly detected toward the CND, but is relatively strong in the starburst ring.

(ii) At present, some molecules have been found to be separated into eastern and western knots in the CND with interferometric observations, and similar distributions of \textsuperscript{13}CO (\textit{J} = 3–2), CN (\textit{N} = 3–2), and CS (\textit{J} = 7–6) are found in our observations for the first time.

(iii) We have determined rotation diagrams of observed molecules in the 3-mm band (Paper 1) and 0.8-mm band (this work) toward the CND and the southwest position in the starburst ring. The rotational temperatures and column densities have been calculated from these diagrams. \textsuperscript{13}CO and C\textsuperscript{18}O molecules trace cold gas (< 10 K) in the starburst ring and slightly warmer gas (14.2–21.5 K) in the CND. Although the column densities of the CO isotopic species in the CND are only one-third of that in the starburst ring, those of the shock-/dust-related molecules are enhanced by a factor of 3–4 in the CND under the assumption of the same \textit{T}_{\text{rot}} in the CND and starburst ring. If \textit{T}_{\text{rot}} is higher in the CND than in the starburst ring, the column density of the shock-related molecules, such as HNCO, CH\textsubscript{3}CN, SO, and CH\textsubscript{3}OH, is much larger in the CND than in the starburst ring.

(iv) The difference of the distributions between \textsuperscript{13}CO and C\textsuperscript{18}O is unexplained by only a difference of excitation conditions, because the abundance ratio of these species is not sensitive to the molecular gas temperature and density. The column density ratios of \textsuperscript{13}CO/C\textsuperscript{18}O in the CND and the starburst ring are \textasciitilde 6, under the assumption that \textit{T}_{\text{rot}} = 30 K for C\textsuperscript{18}O and \textasciitilde 3, respectively. The amount of C\textsuperscript{18}O in the CND is smaller than that in the starburst ring as compared with that of \textsuperscript{13}CO. This feature is possibly the result of differences in isotopic ratios and/or the effect of isotope-selective photodissociation.

(v) We found an especially large enhancement of CN in the CND. Specifically, the column density in the CND is a factor of 20–50 larger than that in the starburst ring. CN is one of the key molecules to study an XDR, as mentioned in theoretical studies (e.g., Meijerink et al. 2007; Harada et al. 2013). Moreover the fractional abundance derived in the CND is closer to the value in XDRs and in the shocked region L1157(B1), but higher than that of cold cores or, especially, hot cores. Since a high X-ray luminosity from the AGN is seen, the high abundance of CN seen in the CND can be explained by XDRs. Therefore, the enhancement of column density and abundance of CN in the CND may be the effects of extreme physical conditions such as those in XDRs.

(vi) We discuss the chemistry of each species, and compare the observed abundances in the CND and starburst ring with those of Galactic sources such as cold cores, hot cores, and shocked molecular clouds in order to study the overall characteristics. As a result, the CND of NGC 1068 seems to be chemically very rich. The CND hosts relatively complex molecules, which are often associated with shocked molecular clouds or hot cores. Because a high X-ray flux can dissociate these molecules, they must also reside in regions shielded from X-rays.

\textbf{Note added in proof (2015 January 16):}

After the submission of this manuscript, we found a relevant paper by Viti et al. (2014, A&A, 570, A28). These authors also discussed the chemistry in the circumnuclear disk and the starburst regions of NGC 1068.

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