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

















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# The ALMA Survey of 70 $\mu\text{m}$ Dark High-mass Clumps in Early Stages (ASHES). VII. Chemistry of Embedded Dense Cores

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## Abstract

We present a study of the chemistry toward 294 dense cores in 12 molecular clumps, using data obtained from the ALMA Survey of 70  $\mu\text{m}$  dark High-mass clumps in Early Stages. We identified 97 protostellar cores and 197 prestellar core candidates, based on the detection of outflows and molecular transitions of high upper-energy levels ( $E_u/k > 45$  K). The detection rate of the  $\text{N}_2\text{D}^+$  emission toward the protostellar cores is 38%, which is higher than 9% for the prestellar cores, indicating that  $\text{N}_2\text{D}^+$  does not exclusively trace prestellar cores. The detection rates of the  $\text{DCO}^+$  emission are 35% for the prestellar cores and 49% for the protostellar cores, which are higher than those for  $\text{N}_2\text{D}^+$ , implying that  $\text{DCO}^+$  appears more frequently than  $\text{N}_2\text{D}^+$  in both prestellar and protostellar cores. Both the  $\text{N}_2\text{D}^+$  and  $\text{DCO}^+$  abundances appear to decrease from the prestellar to the protostellar stage. The DCN,  $\text{C}_2\text{D}$ , and  $^{13}\text{CS}$  emission lines are rarely seen in the dense cores of early evolutionary phases. The detection rate of the  $\text{H}_2\text{CO}$  emission toward dense cores is 52%, three times higher than that for  $\text{CH}_3\text{OH}$  (17%). In addition, the  $\text{H}_2\text{CO}$  detection rate, abundance, line intensities, and line widths increase with the core evolutionary status, suggesting that the  $\text{H}_2\text{CO}$  line emission is sensitive to protostellar activity.

*Unified Astronomy Thesaurus concepts:* Infrared dark clouds (787); Star forming regions (1565); Star formation (1569); Massive stars (732); Protostars (1302); Protoclusters (1297); Interstellar medium (847); Interstellar line emission (844); Astrochemistry (75)

*Supporting material:* machine-readable table

## 1. Introduction

The chemical compositions of planets are affected by the chemical makeups of the protoplanetary disks within which they form. The chemical contents of the prestellar and protostellar cores set the initial conditions in protoplanetary disks (Caselli & Ceccarelli 2012; Drozdovskaya et al. 2019; Jørgensen et al. 2020; Booth et al. 2021; Öberg & Bergin 2021). Molecular lines are a powerful tool for revealing the chemical and physical processes during star formation and core evolution, since different molecules can be associated with specific chemical and physical environments (Bergin & Tafalla 2007). Consequently, different molecular lines can be used to probe different gas environments, i.e., different physical

conditions. For instance, deuterated molecules (e.g.,  $\text{N}_2\text{D}^+$ ,  $\text{DCO}^+$ ,  $\text{H}_2\text{D}^+$ , and  $\text{NH}_2\text{D}$ ) can be used to trace cold and dense molecular clumps/cores associated with early evolutionary stages of star formation (e.g., prestellar cores; Caselli et al. 2002; Kong et al. 2017; Giannetti et al. 2019; Sabatini et al. 2020; Li et al. 2021; Redaelli et al. 2021; Sakai et al. 2022). On the other hand, high-density gas tracers could also suffer from depletion toward cold and dense regions (e.g.,  $\text{N}_2\text{H}^+$ —Pagani et al. 2007;  $\text{N}_2\text{D}^+$ —Redaelli et al. 2019;  $\text{NH}_3$ —Pineda et al. 2022). A prestellar core would further evolve into a protostellar core, in which protostars launch molecular outflows and heat the surrounding material. These physical processes can cause molecules to be released from the grain surface to the gas phase, causing the enhancement of various molecules in the gas phase (van Dishoeck & Blake 1998; Herbst & van Dishoeck 2009). CO and SiO are frequently used to probe protostellar activities (e.g., Sanhueza et al. 2010, 2017; Li et al. 2019, 2020; Lu et al. 2021), i.e., molecular jets and outflows. Formaldehyde ( $\text{H}_2\text{CO}$ ) and methanol ( $\text{CH}_3\text{OH}$ ) are commonly seen in star-

forming regions, and their abundances can be significantly enhanced with respect to quiescent regions in the presence of protostellar activity (e.g., molecular outflows; Arce et al. 2008; Sakai et al. 2012; Sanhueza et al. 2013; Jørgensen et al. 2020; Morii et al. 2021; Tychoniec et al. 2021). In addition, both species play key roles in the formation of more complex organic molecules, such as amino acids and other prebiotic molecules (Bernstein et al. 2002; Muñoz Caro et al. 2002; Garrod et al. 2008; Guzmán et al. 2013), which might be transported to circumstellar disks and potential planetary systems (Drozdovskaya et al. 2019). Thus, a full understanding of the chemical properties of star-forming clouds is essential for improving our knowledge of the physical and chemical processes that take place during star formation.

Numerous observational investigations have aimed at understanding the chemistry of star-forming molecular clouds. For instance, single pointing observations of a sample of massive clumps using single-dish telescopes (e.g., infrared dark clouds, or IRDCs—Sanhueza et al. 2012; Vasyunina et al. 2014; IRDCs to hot cores—Gerner et al. 2014; Sabatini et al. 2021), single-dish mapping of a sample of massive clumps (e.g., IRDCs—Miettinen 2014; IRDCs to H II regions—Hoq et al. 2013), interferometer/single-dish observations toward several massive clumps (e.g., IRDCs—Feng et al. 2020; H II regions—Li et al. 2017), interferometer observations of a sample of H II regions (Qin et al. 2022), and case studies (e.g., Sanhueza et al. 2013; Immer et al. 2014; Liu et al. 2020; Peng et al. 2022). Thanks to these observational studies of chemistry toward different star formation regions, our understanding of chemistry has been significantly advanced; for instance, chemical abundances of molecular species vary significantly throughout the evolutionary sequence of star-forming regions.

Despite these advances, the chemical properties of prestellar and protostellar cores are still unclear, due to the lack of observations of a large sample of dense cores at early evolutionary stages. Here, we use Atacama Large Millimeter/submillimeter Array (ALMA) high-sensitivity and high-spatial resolution data to investigate the chemistry of a statistically significant sample ( $N = 294$ ) of spatially resolved deeply embedded dense cores, which are still at extremely early evolutionary stages of star formation. The data were obtained by the ALMA Survey of 70  $\mu\text{m}$  dark High-mass clumps in Early Stages (ASHES), first presented in Sanhueza et al. (2019; hereafter, Paper I). The molecular outflow content and the CO depletion fraction of the detected ASHES cores are presented in Li et al. (2020; hereafter, Paper II) and Sabatini et al. (2022), respectively. Case studies are presented in Tafoya et al. (2021), Morii et al. (2021), and Sakai et al. (2022).

Among the 294 dense cores revealed in the continuum emission, we have identified 197 prestellar core candidates (hereafter, prestellar cores) and 97 protostellar cores. The numbers of prestellar and protostellar cores have been updated, thus they are slightly different from the 210 prestellar and 84 protostellar cores reported in Paper I. A core is classified as “prestellar” (category 1) if it is not associated with molecular outflows and/or emission from any of the three lines  $\text{CH}_3\text{OH } 4_{2,2} - 3_{1,2}$  ( $E_u/k = 45.46$  K),  $\text{H}_2\text{CO } 3_{2,2} - 2_{2,1}$  ( $E_u/k = 68.09$  K), or  $\text{H}_2\text{CO } 3_{2,1} - 2_{2,0}$  ( $E_u/k = 68.11$  K). A core is classified as an “outflow core” (category 2) if it is associated with outflows detected in the molecular line emission, but without the detection of any of the three aforementioned lines (Paper II). Details of the molecular outflows are presented in Paper II.

A core is classified as a “warm core” (category 3) if it is associated with emission from any of the three aforementioned lines, but without outflow detection. The “warm core” refers to an evolutionary stage prior to the “hot-core” phase. A core is classified as an “outflow + warm core” (category 4) if it is associated with emission from any of the three aforementioned lines, as well as with outflows. Overall, categories 2, 3, and 4 are considered as protostellar cores.

In this work, we study the chemistry of embedded dense cores in the extremely early evolutionary stages of high-mass star-forming regions, using high-angular resolution and high-sensitivity ALMA observations. With a statistically significant sample of dense cores, we will study the properties of deuterated molecules ( $\text{N}_2\text{D}^+$ ,  $\text{DCO}^+$ ,  $\text{C}_2\text{D}$ , and  $\text{DCN}$ ) and dense gas tracers ( $\text{C}^{18}\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , and  $^{13}\text{CS}$ ). The paper is organized as follows. Section 2 describes the observations. The results and analysis are presented in Section 3. In Section 4, we discuss the results. A summary of the main conclusions is presented in Section 5.

## 2. Observations

Observations of 12 70  $\mu\text{m}$  dark molecular clumps were performed with ALMA in Band 6 ( $\sim 224$  GHz; 1.34 mm), using the main 12 m array, the 7 m array, and the total power array (TP; Project ID: 2015.1.01539.S, PI: P. Sanhueza). The mosaic observations were carried out with the 12 m array and 7 m array, to cover a significant portion of the clumps, as defined by single-dish continuum images. The same correlator setup was applied for all sources. More details on the observations can be found in Papers I and II.

Data calibration was performed using the CASA software package, versions 4.5.3, 4.6, and 4.7, while the 12 m and 7 m array data sets were concatenated and imaged together using the CASA 5.4 `tclean` algorithm (McMullin et al. 2007). Data cubes for lines were produced using the `yclean` script, which automatically cleans each map channel with custom-made masks (Contreras et al. 2018). The imaging process uses two times the  $\sigma$  rms threshold. The continuum emission was obtained by averaging the line-free channels in visibility space. We used a multiscale clean for the continua and data cubes, with scale values of 0, 5, 15, and 25 times the image pixel size of  $0''.2$ . Since some sources were observed with different configurations, a uv taper was used for such sources, in order to obtain a similar synthesized beam of  $\sim 1''.2$  for all sources. We adopted Briggs robust weightings of 0.5 and 2 for the visibilities of the continua and the lines in the imaging process, respectively. This achieved an averaged  $1\sigma$  noise level of  $\sim 0.1$  mJy beam $^{-1}$  for the continuum images. For the detected molecular lines ( $\text{N}_2\text{D}^+ J = 3-2$ ,  $\text{DCN } J = 3-2$ ,  $\text{DCO}^+ J = 3-2$ ,  $\text{C}_2\text{D } J = 3-2$ ,  $^{13}\text{CS } J = 5-4$ ,  $\text{SiO } J = 5-4$ ,  $\text{C}^{18}\text{O } J = 2-1$ ,  $\text{CO } J = 2-1$ ,  $\text{CH}_3\text{OH } 4_{2,2} - 3_{1,2}$ , and  $\text{H}_2\text{CO } 3_{0,3} - 2_{0,2}$ ,  $3_{2,2} - 2_{2,1}$ , and  $3_{2,1} - 2_{2,0}$ ), the sensitivities are  $\sim 9.5$  mJy beam $^{-1}$  per  $0.17$  km s $^{-1}$  for the first six lines and  $\sim 3.5$  mJy beam $^{-1}$  per  $1.3$  km s $^{-1}$  for the last six lines (see Table 1). The 12 m and 7 m array line emissions were combined with the TP observations through the feathering technique. All images shown in this paper are prior to primary beam correction, while all measured fluxes are corrected for primary beam attenuation.

**Table 1**  
Summary of Detected Lines and Their Parameters

Molecule	Transition	Frequency (GHz)	$E_u/k$ (K)	$S_{ij}\mu^2$ D <sup>2</sup>	$n_{\text{crit}}$ (cm <sup>-3</sup> )	$Q_{\text{rot}}$	Rotational Constants (MHz)	Beam Size (")	rms
DCO <sup>+</sup>	3 – 2	216.112	20.74	45.624	1.84E+06	$0.58T_{\text{ex}} + 0.34$		$1.5 \times 1.0$	9.5 <sup>a</sup>
C <sub>2</sub> D	3 – 2	216.373	20.77	2.541	8.18E+05	$3.47T_{\text{ex}} + 2.06$		$1.6 \times 1.0$	9.5 <sup>a</sup>
SiO	5 – 4	217.105	14.48	48.146	1.22E+06	$\frac{k_B T_{\text{ex}}}{h B_0} + \frac{1}{3}$	$B_0 = 21711.97$	$1.6 \times 1.0$	9.5 <sup>a</sup>
DCN	3 – 2	217.238	20.85	80.501	2.16E+07	$0.1T_{\text{ex}}^{3/2} + 50.51$		$1.7 \times 1.0$	9.5 <sup>a</sup>
p-H <sub>2</sub> CO	3 <sub>0,3</sub> – 2 <sub>0,2</sub>	218.222	20.95	16.308	2.56E+06	$\frac{1}{3} \left( \frac{\pi k_B^3 T_{\text{ex}}^3}{h^3 A_0 B_0 C_0} \right)^{0.5}$	$A_0 = 281970.56$	$1.5 \times 1.0$	3.5 <sup>b</sup>
p-H <sub>2</sub> CO	3 <sub>2,2</sub> – 2 <sub>2,1</sub>	218.475	68.09	9.062	2.96E+06		$B_0 = 38833.987$	$1.5 \times 1.0$	3.5 <sup>b</sup>
p-H <sub>2</sub> CO	3 <sub>2,1</sub> – 2 <sub>2,0</sub>	218.76	68.11	9.062	3.36E+06		$C_0 = 34004.244$	$1.5 \times 1.0$	3.5 <sup>b</sup>
CH <sub>3</sub> OH	4 <sub>2,2</sub> – 3 <sub>1,2</sub>	218.44	45.46	13.906	2.04E+07	$\frac{1}{2} \left( \frac{\pi k_B^3 T_{\text{ex}}^3}{h^3 A_0 B_0 C_0} \right)^{0.5}$	$A_0 = 127523.4$	$1.5 \times 1.0$	3.5 <sup>b</sup>
							$B_0 = 24690.2$		
							$C_0 = 23759.7$		
C <sup>18</sup> O	2 – 1	219.56	15.81	0.024	9.33E+03	$\frac{k_B T_{\text{ex}}}{h B_0} + \frac{1}{3}$	$B_0 = 54891.42$	$1.5 \times 1.0$	3.5 <sup>b</sup>
<sup>13</sup> CS	5 – 4	231.22	32.73	38.335	4.46E+06	$1.85T_{\text{ex}} - 3.32$		$1.4 \times 1.0$	9.5 <sup>a</sup>
N <sub>2</sub> D <sup>+</sup>	3 – 2	231.321	22.2	312.104	1.70E+06	$4.87T_{\text{ex}} + 2.81$		$1.5 \times 1.0$	9.5 <sup>a</sup>

**Note.**  $E_u/k$  and  $S_{ij}\mu^2$  are obtained from the Cologne Database for Molecular Spectroscopy (<https://cdms.astro.uni-koeln.de/cdms/portal/>; Müller et al. 2005). The critical densities are estimated using the equation  $n_{\text{crit}} = A_{ul}/\gamma$ , where Einstein A coefficients ( $A_{ul}$ ) and collisional rates ( $\gamma$ ) at 20 K were obtained from the Leiden atomic and molecular database (Schöier et al. 2005). For N<sub>2</sub>D<sup>+</sup>, DCN, and C<sub>2</sub>D, we use the same collision rates as for N<sub>2</sub>H<sup>+</sup>, HCN, and C<sub>2</sub>H, respectively, since the lack of direct experimental constraints and the transitions between the deuterated and nondeuterated isotopologue do not differ significantly. The collision rate value of <sup>13</sup>CS is from its main isotopologue. The rotational constants (i.e.,  $A_0$ ,  $B_0$ ,  $C_0$ ) are retrieved from the splatalogue database for astronomical spectroscopy (<https://splatalogue.online/>). a: the unit is mJy beam<sup>-1</sup> per 0.17 km s<sup>-1</sup>. b: the unit is mJy beam<sup>-1</sup> per 1.3 km s<sup>-1</sup>.

### 3. Results and Analysis

At the moment, the ALMA TP antennas do not provide continuum emission observations. Therefore, our analysis of the continua and molecular lines is mostly focused on combined 12 m and 7 m images (hereafter, 12m7m), whereas the combined 12 m, 7 m, and TP images (hereafter, 12m7mTP) are used to assess the missing flux in images without TP data.

The `astropy astrodendro` package (Rosolowsky et al. 2008; Astropy Collaboration et al. 2013) was employed to identify the embedded dense cores for each clump (Paper I). A minimum value of  $2.5\sigma$ , a step of  $1.0\sigma$ , and a minimum number of pixels equal to those contained in half of each synthesized beam were used to extract the dense cores (i.e., the leaves, in the terminology of `astrodendro`). To eliminate spurious detections, we only considered cores with integrated flux densities  $>3.5\sigma$  (see Section 4.2 in Paper I for more details of the identification of dense cores).

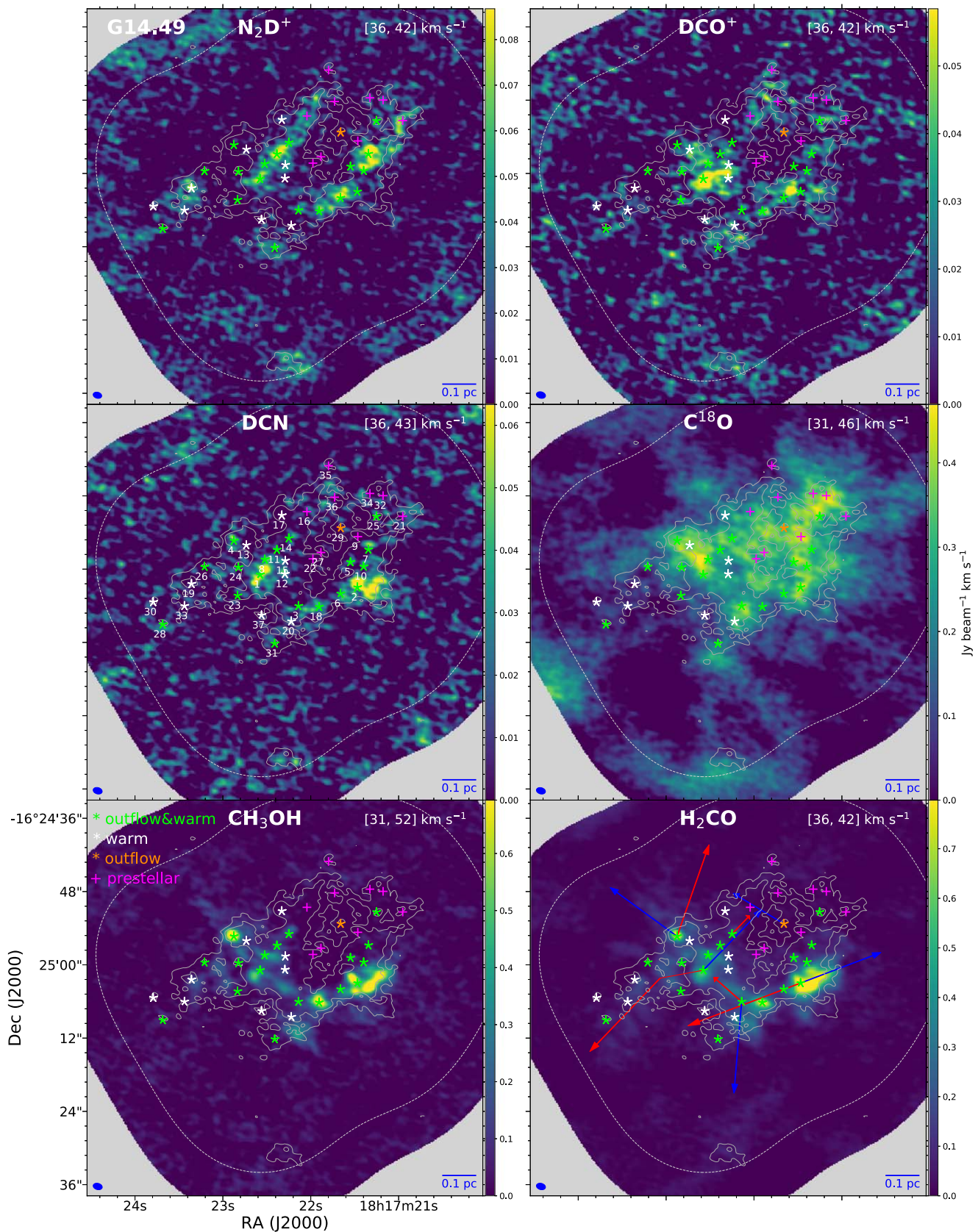
Figure 1 shows the velocity-integrated intensity (also known as 0th-moment) maps of N<sub>2</sub>D<sup>+</sup>, DCO<sup>+</sup>, DCN, H<sub>2</sub>CO (3<sub>0,3</sub> – 2<sub>0,2</sub>), CH<sub>3</sub>OH, and C<sup>18</sup>O for G014.492–00.139 (hereafter, G14.49), but excluding C<sub>2</sub>D, <sup>13</sup>CS, CO, and SiO. The 0th-moment images of molecular lines for the remaining clumps are presented in Appendix A. Among the three H<sub>2</sub>CO transitions, we focus on the H<sub>2</sub>CO (3<sub>0,3</sub> – 2<sub>0,2</sub>) line, unless otherwise noted. H<sub>2</sub>CO (3<sub>0,3</sub> – 2<sub>0,2</sub>) traces cold dense gas better than the other two transitions, 3<sub>2,2</sub> – 2<sub>2,1</sub> and 3<sub>2,1</sub> – 2<sub>2,0</sub>, which preferentially trace warm dense gas. The C<sub>2</sub>D and <sup>13</sup>CS lines are only detected in very limited regions toward 10 dense cores. The spatial distributions of the CO and SiO lines can be found in Paper II. Both the CO and C<sup>18</sup>O lines show significant emission throughout the clumps, although there is a significant depletion in their emission toward some dense cores. Both N<sub>2</sub>D<sup>+</sup> and DCO<sup>+</sup> lines are preferentially present around or toward the dense cores. CH<sub>3</sub>OH and H<sub>2</sub>CO emission lines are frequently

found around outflows and dense cores. The majority of the DCN line emission appears toward the protostellar cores.

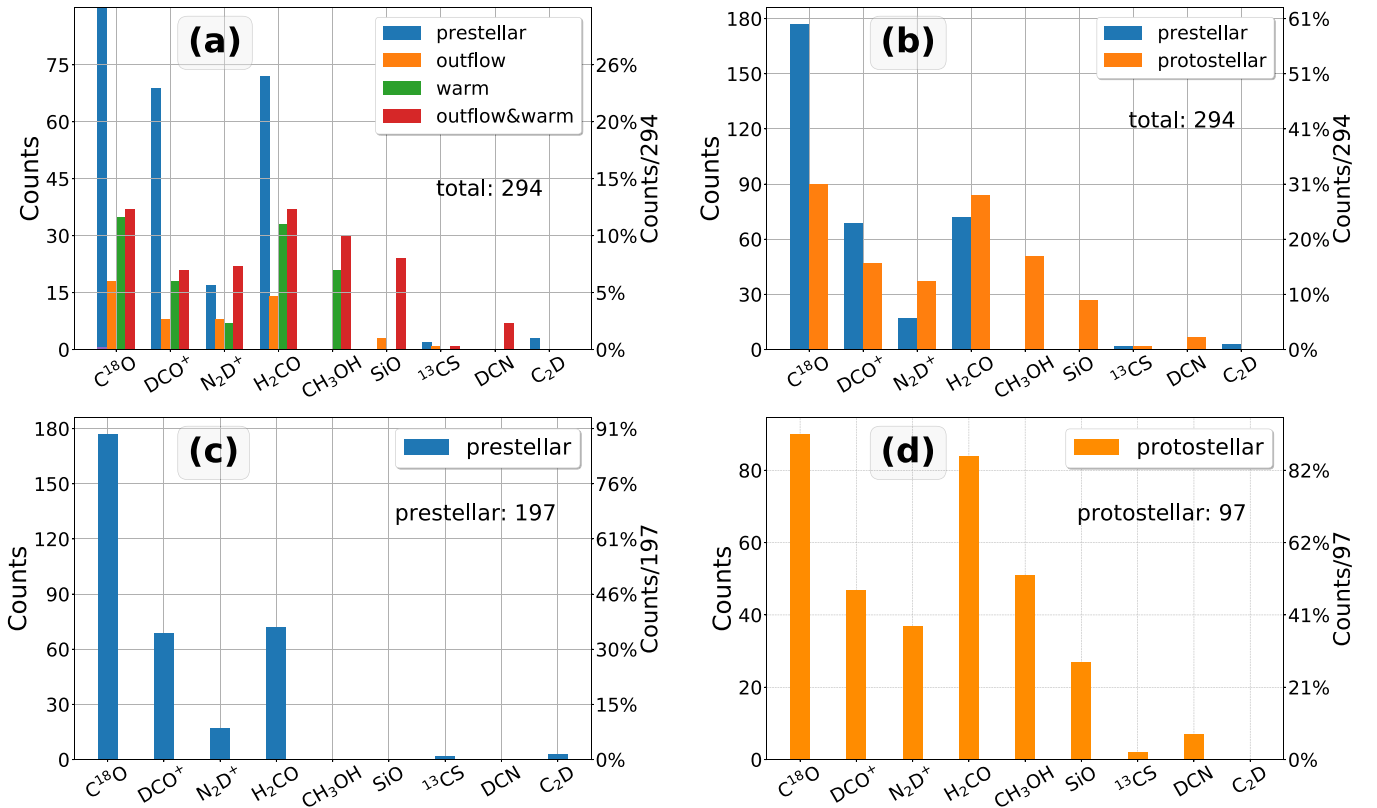
#### 3.1. Detection Rates

In general, the emission from deuterated species is weak. For all the detected lines of interest, the spectra are averaged inside the dendrogram leaf (see Paper I) that defines each core, in order to increase the signal-to-noise ratio (S/N). We derive the line central velocity ( $v_{\text{LSR}}$ ), the observed velocity dispersion ( $\sigma_{\text{obs}} = \text{FWHM}/2\sqrt{2 \ln 2}$ ), and peak intensity ( $I$ ) from Gaussian fittings to the core-averaged spectrum for each line, except for N<sub>2</sub>D<sup>+</sup>, which is fitted with a hyperfine structure (hfs) model. The derived  $\sigma_{\text{obs}}$  is not corrected by the smearing effect, due to the channel width. To increase the S/N of the weak line emission, the core-averaged spectrum is spectrally smoothed over two native channels, prior to Gaussian/hfs fittings, if it shows marginal  $\sim 3\sigma$  confidence in the native spectral resolution. The best-fit parameters, which are used to compute the column densities of molecules (see Appendix C) and the following analyses, are summarized in Appendix A.

CO emission is detected in all the identified cores. C<sup>18</sup>O is detected in 267 of the 294 cores, with a detection rate of 89%. H<sub>2</sub>CO is the third most commonly detected line, which is detected in 156 of the 294 cores, with a detection rate of 52%. CH<sub>3</sub>OH is detected in 51 of the 294 cores, leading to a detection rate of 17%. Among the detected deuterated species, DCO<sup>+</sup> is the most commonly detected line, with a detection rate of 39% (116/294). N<sub>2</sub>D<sup>+</sup> is detected in 54 of the 294 cores, resulting in a detection rate of 18%. There are seven cores that are associated with the DCN line emission, with a detection rate of 2%. There is weak C<sub>2</sub>D emission in three dense cores, with a detection rate of 1%. <sup>13</sup>CS is detected toward four dense cores, with a detection rate of 1%. Based on the core-averaged spectra, SiO emission is detected in 27 cores.



**Figure 1.** The velocity-integrated intensity maps of the  $\text{N}_2\text{D}^+$ ,  $\text{DCO}^+$ ,  $\text{DCN}$ ,  $\text{C}^{18}\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2\text{CO}$  emission lines toward G14.49. The unit of the colorbar is  $\text{Jy beam}^{-1} \text{ km s}^{-1}$ . The fuchsia pluses and yellow, white, and green asterisks indicate prestellar candidates (category 1), outflow cores (category 2), warm cores (category 3), and outflow + warm cores (category 4). The white dashed line shows 30% of the sensitivity level of the mosaic in the ALMA continuum image. The blue and red arrows in the bottom right panel indicate the directions of the blueshifted and redshifted CO outflow lobes (see Paper II), respectively. The gray contours in each panel show the 1.3 mm continuum emission. The contour levels are  $(3, 6) \times \sigma$ , with  $\sigma = 0.115 \text{ mJy beam}^{-1}$ . The beam sizes of the line emissions and scale bars are shown in the lower left and right corners of each panel, respectively. The remaining sources are presented in Appendix A (see Figures 10–14).



**Figure 2.** Histograms of the number and detection rate distributions of detected lines for: each evolutionary category of cores (a); prestellar vs. protostellar cores (b); prestellar cores only (c); and protostellar cores only (d).

Figure 2 shows histograms of the number distributions and detection rates of the detected lines for the prestellar cores, protostellar cores, and for each core category.  $N_2D^+$  is detected in 17 prestellar cores and 37 protostellar cores, resulting in a detection rate in the prestellar phase ( $9\% = 17/197$ ) lower than that in the protostellar phase ( $38\% = 37/97$ ). The high  $N_2D^+$  detection rate for the protostellar cores indicates that  $N_2D^+$  does not exclusively trace prestellar cores and that it also frequently appears in protostellar cores (Giannetti et al. 2019). Among the detected deuterated molecules,  $DCO^+$  has the highest detection rate in both the prestellar and protostellar cores. The  $DCO^+$  detection rates are  $35\%$  ( $69/197$ ) and  $49\%$  ( $47/97$ ) for the prestellar and protostellar cores (Figure 2), respectively. This indicates that  $DCO^+$  is more frequently detected than  $N_2D^+$  in both the prestellar and protostellar cores.

The  $H_2CO$  detection rate in the protostellar cores ( $87\% = 84/97$ ) is more than twice that in the prestellar cores ( $37\% = 72/197$ ). On the other hand,  $H_2CO$  has a higher detection rate than  $N_2D^+$  in both the prestellar and protostellar cores, indicating that  $H_2CO$  is more commonly seen than the  $N_2D^+$  emission in these dense cores at early evolutionary phases. There are 51 ( $53\% = 51/97$ ) protostellar cores showing  $CH_3OH$  line emission.  $DCN$  is detected in seven protostellar cores.  $C_2D$  is detected in three prestellar cores.  $^{13}CS$  is detected in two prestellar and two protostellar cores. The detection numbers and detection rates of each line for all of the categories are summarized in Table 2.

### 3.2. Spatial Distributions of Line Emissions

In general, both CO and  $C^{18}O$  show the most spatially extended emission over all clumps, followed by  $H_2CO$  and

$CH_3OH$ , and then by  $DCO^+$ ,  $N_2D^+$ ,  $SiO$ ,  $DCN$ ,  $^{13}CS$ , and  $C_2D$ . From Figure 1 (see also Appendix A), we note that the  $C^{18}O$  emission is extended in the IRDC clumps. There is very weak  $C^{18}O$  emission toward some of the dense cores, likely due to depletion (e.g., cores #28 and #30 in G14.49; see also Sabatini et al. 2022).

$N_2D^+$  shows extended emission toward dense cores. The peaks of the  $N_2D^+$  emission are offset from the continuum peaks in some cores, with a significant decrease in intensity toward the continuum emission peaks (e.g., cores #8 and #2 in G14.49; see Figure 1). Both  $N_2$  depletion and CO evaporation toward the centers of the cores can lead to a decrease in  $N_2D^+$  abundance. We are unable to distinguish between these two possibilities with the current data.  $DCO^+$  also shows extended emission toward the dense cores. However, the spatial distribution of  $DCO^+$  does not always coincide with that of  $N_2D^+$  (see, for example, Sakai et al. 2022). For instance,  $DCO^+$  shows a significantly different spatial distribution from what is observed for  $N_2D^+$  around cores #7, #10, and #21 in G14.49 (see Figure 1).

The peaks of the  $H_2CO$  and  $CH_3OH$  emission appear either to coincide with the continuum peaks or to be located in the direction of the outflows in the majority of cases (Figure 1 and Appendix A). The  $CH_3OH$  emission shows a behavior similar to what is observed for  $H_2CO$ , but with less extended emission. This is most likely due to the fact that the excitation conditions of  $H_2CO$  ( $3_{0,3} - 2_{0,2}$ ) are different from those of  $CH_3OH$  (e.g., lower upper-level energies and critical densities; see Table 1).

There are some pairs of molecules that show similar spatial distributions in some clumps, e.g.,  $H_2CO$  and  $CH_3OH$ . To compare the spatial trends of different species, we performed a

**Table 2**  
Detection Rates

Molecules	Prestellar	Outflow Core	Protostellar Warm Core	Outflow + Warm Core	Sum	All
Total Number	197	21	37	37	97	294
C <sup>18</sup> O	177 (89.8%)	18 (85.7%)	35 (94.6%)	37 (94.9%)	90 (92.8%)	267 (90.8%)
DCO <sup>+</sup>	69 (35.0%)	8 (38.1%)	18 (48.6%)	21 (53.8%)	47 (48.5%)	116 (39.5%)
N <sub>2</sub> D <sup>+</sup>	17 (8.6%)	8 (38.1%)	7 (18.9%)	22 (56.4%)	37 (38.1%)	54 (18.4%)
H <sub>2</sub> CO	72 (36.5%)	14 (66.7%)	33 (89.2%)	37 (94.9%)	84 (86.6%)	156 (53.1%)
CH <sub>3</sub> OH	...	...	21 (56.8%)	30 (76.9%)	51 (52.6%)	51 (17.3%)
SiO	...	3 (14.3%)	...	24 (61.5%)	27 (27.8%)	27 (9.2%)
<sup>13</sup> CS	2 (1.0%)	1 (4.8%)	...	1 (2.6%)	2 (2.1%)	4 (1.4%)
DCN	...	...	...	7 (17.9%)	7 (7.2%)	7 (2.4%)
C <sub>2</sub> D	3 (1.5%)	...	...	...	...	3 (1.0%)

half-beam sampling for the 0th moment of each molecular line. Each data point (or pixel) is about half the beamwidth, to ensure that data points are not oversampled. The similarity of the 0th-moment maps of different molecules can be evaluated quantitatively by the cross correlation between each pair of maps, according to Guzmán et al. (2018):

$$\rho_{12} = \frac{\sum_{i,j} I_{1,ij} I_{2,ij} w_{ij}}{\left(\sum_{i,j} I_{1,ij}^2 w_{ij} \sum_{i,j} I_{2,ij}^2 w_{ij}\right)^{1/2}}, \quad (1)$$

where the sums are taken over all positions.  $I_{1,ij}$  and  $I_{2,ij}$  are the integrated intensities at the position  $i, j$  for two arbitrary species, 1 and 2, respectively, and the weight  $w_{ij}$  is equal to 0 or 1, depending on whether or not the line emission was detected at that position.  $\rho_{12}$  is equal to 1 if the 0th-moment maps of two molecules have the same spatial distribution. Although some pairs of molecules that show weak emission do not have statistically significant numbers of independent data points, they are still worth examining. To alleviate the effect of insufficient numbers of independent data points for comparison, we avoid deriving the correlation coefficients of pairs of molecules whose overlapping emitting areas are smaller than one synthesized beam.

Figure 3 presents cross-correlation coefficients for the 0th-moment maps for each pair of molecules. The correlation between N<sub>2</sub>D<sup>+</sup> and DCO<sup>+</sup> is better than those for the other detected deuterated molecules (i.e., DCN and C<sub>2</sub>D) in all the clumps. This is because the emitting regions of the DCN and C<sub>2</sub>D lines are smaller than those for either N<sub>2</sub>D<sup>+</sup> or DCO<sup>+</sup> (Figure 1). The DCO<sup>+</sup> line emission coincides better with H<sub>2</sub>CO and CH<sub>3</sub>OH than N<sub>2</sub>D<sup>+</sup> in terms of spatial distribution. This may be because DCO<sup>+</sup>, H<sub>2</sub>CO, and CH<sub>3</sub>OH have a common precursor molecule of CO that tends to destroy N<sub>2</sub>D<sup>+</sup> (see Sections 4.2 and 4.3).

In general, the CH<sub>3</sub>OH and H<sub>2</sub>CO emissions have the most similar spatial distributions in integrated intensities, with the highest correlation coefficients among the detected lines. Most of the CH<sub>3</sub>OH and H<sub>2</sub>CO emissions appear to be around either outflows or dense cores (Figure 1). In addition, both the CH<sub>3</sub>OH and H<sub>2</sub>CO emissions show good spatial correlation with the SiO emission in most of the clumps (Figure 3). These results suggest that both the CH<sub>3</sub>OH and H<sub>2</sub>CO line emissions are closely related to the outflow activity toward protostellar cores in the ASHES clumps.

### 3.3. Molecular Line Parameters

Figure 4 shows the distribution of the derived  $I$  and  $\sigma_{\text{obs}}$  of each line for the prestellar and protostellar cores (see also Table 3). Overall,  $\sigma_{\text{obs}}$  shows no significant difference between the prestellar and protostellar cores for the C<sup>18</sup>O and DCO<sup>+</sup> emissions. This indicates that the protostellar cores are still at a very early evolutionary phase, in which the line widths of C<sup>18</sup>O (a low-density gas tracer) and DCO<sup>+</sup> (a high-density tracer) have not been significantly affected by protostellar activity. In general, the N<sub>2</sub>D<sup>+</sup> line has a comparable  $I$  in both the prestellar and protostellar cores, except for four protostellar cores that present a relatively higher  $I$  than for the prestellar cores. On the other hand, the N<sub>2</sub>D<sup>+</sup> line emission shows a relatively larger  $\sigma_{\text{obs}}$  in the protostellar cores compared with the prestellar cores. This might be because the N<sub>2</sub>D<sup>+</sup> line emission toward the protostellar cores is influenced by the injection of turbulence, as a result of protostellar activity.

For the H<sub>2</sub>CO emission, both  $I$  and  $\sigma_{\text{obs}}$  in the protostellar cores are higher than in the prestellar cores. This is because H<sub>2</sub>CO abundances can be significantly enhanced in warm and dense environments, and its line width can be broadened by protostellar activity (e.g., outflows; Tafalla et al. 2010; Sakai et al. 2012). In addition, H<sub>2</sub>CO is the molecule in our sample that shows a clearly increasing trend in both  $I$  and  $\sigma_{\text{obs}}$  for categories 1 to 4 (see Figure 4), indicating that its abundance and line width are sensitive to the evolution of the dense cores. This implies that H<sub>2</sub>CO could be used as a diagnostic tool for inferring star formation activities.

From Figure 4, one notes that the H<sub>2</sub>CO ( $\langle\sigma_{\text{obs}}\rangle = 1.68 \text{ km s}^{-1}$ ) and CH<sub>3</sub>OH ( $\langle\sigma_{\text{obs}}\rangle = 1.82 \text{ km s}^{-1}$ ) lines show relatively larger  $\sigma_{\text{obs}}$  than C<sup>18</sup>O ( $\langle\sigma_{\text{obs}}\rangle = 0.99 \text{ km s}^{-1}$ ), DCO<sup>+</sup> ( $\langle\sigma_{\text{obs}}\rangle = 0.35 \text{ km s}^{-1}$ ), and N<sub>2</sub>D<sup>+</sup> ( $\langle\sigma_{\text{obs}}\rangle = 0.25 \text{ km s}^{-1}$ ) toward the protostellar cores (see also Table 3). This could be because H<sub>2</sub>CO and CH<sub>3</sub>OH are associated with more turbulent gas components that are affected by protostellar activity (e.g., outflows; Tychoniec et al. 2021). We refrain from investigating  $I$  and  $\sigma_{\text{obs}}$  for the <sup>13</sup>CS, DCN, and C<sub>2</sub>D emissions, due to the lack of a sufficient number of detections for a meaningful analysis, as well as the SiO emission, which is mainly associated with outflows.

### 3.4. Derivation of Physical Parameters

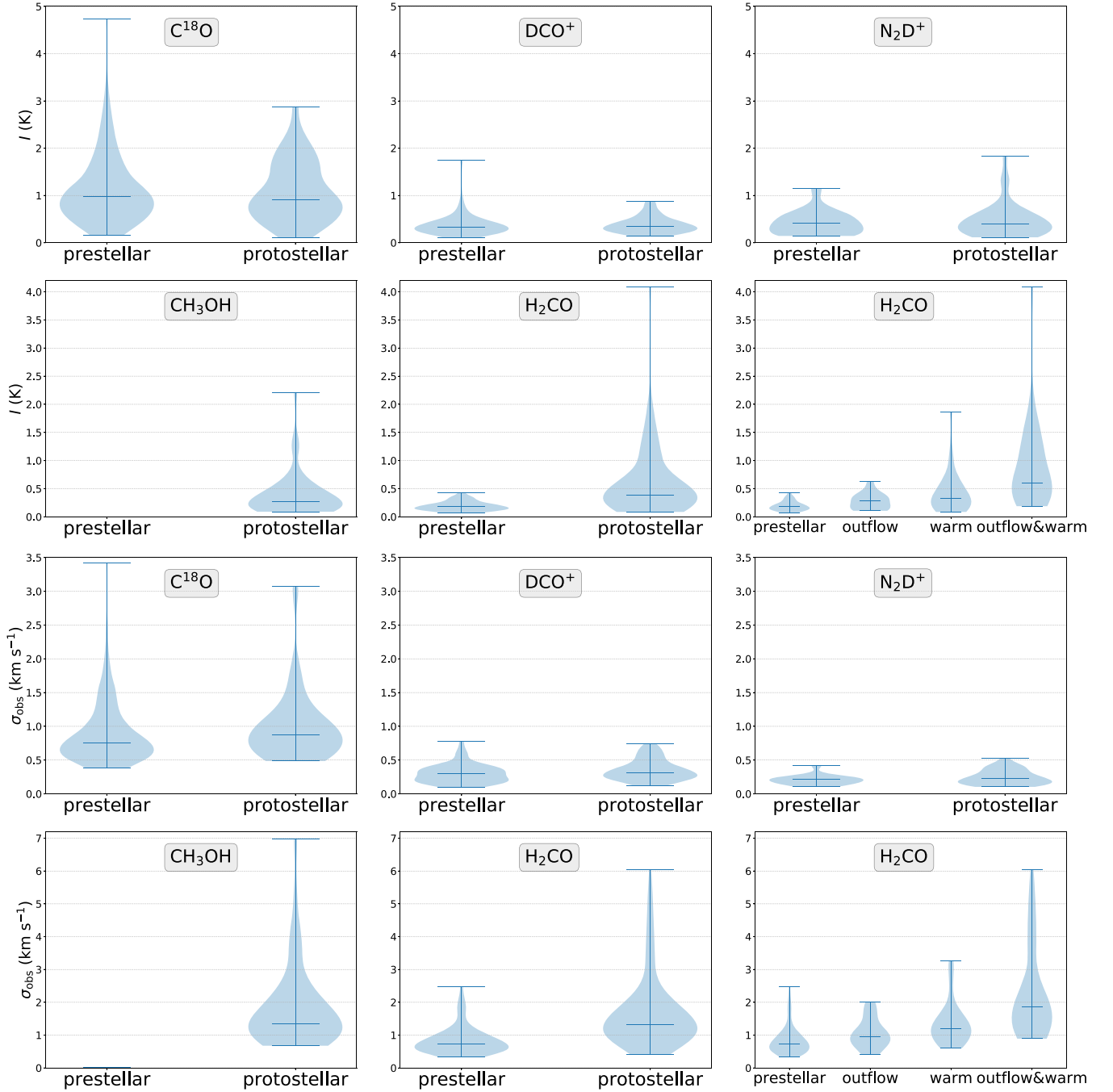
The rotational excitation temperature ( $T_{\text{NH}_3}$ ) is derived from NH<sub>3</sub> (1, 1) and (2, 2) transition lines obtained from the CACHMC survey (Complete ATCA<sup>16</sup> Census of High-Mass Clumps; D. Allingham et al. 2022, in preparation) at  $\sim 5''$

<sup>16</sup> The Australia Telescope Compact Array.



**Figure 3.** Integrated intensity correlation matrix, showing cross correlations for each pair of molecules. The correlation coefficients are described in the text. The “+” symbols mean that correlation coefficients cannot be derived, either due to lack of detection or the spatially overlapped emitting area being smaller than one beam in size. The colors indicate the number of beam areas of the spatially overlapping emitting regions. Larger numbers of beam areas have more robust derived correlation coefficients than smaller ones.





**Figure 4.** Violin plots of the peak intensity  $I$  and observed velocity dispersion  $\sigma_{obs}$  distributions for each line. The shape of each distribution shows the probability density of the data, smoothed by a kernel density estimator. The last panel shows the  $H_2CO$  peak intensity distributions of each category of dense cores. The blue horizontal bars from the top to bottom of each violin plot represent the maximum, mean, and minimum values, respectively.

angular resolution (see Appendix B for the detailed procedure for the excitation temperature determination). More details of the procedure for the temperature determination and the survey results will be presented in a forthcoming paper (D. Allingham et al. 2022, in preparation). The derived  $T_{NH_3}$  is used as the excitation temperature in the calculation of all molecular parameters, except for G332.96, which has no available  $NH_3$  data. We used the dust temperature at the clump scale of 12.6 K for G332.96 (Paper I). The averaged temperatures of the dense cores in the same category for a given clump are used for those dense cores that have no available  $T_{NH_3}$ . The approximation of using  $T_{NH_3}$  as the excitation temperature is based on the local

thermodynamic equilibrium (LTE) conditions in the calculation of the molecular density. The results could be highly sensitive to the choice of the excitation temperature.

Using these new temperatures, we have recalculated the ASHES cores properties. The analysis of how these new core properties affect the analysis presented in Paper I will be presented in a forthcoming paper (S. Li et al. 2022, in preparation). For the chemical analysis of the current work, we have used the updated core-averaged  $H_2$  column densities and core volume densities (see Appendix C). The updated parameters are  $4.9 \times 10^{21} - 2.0 \times 10^{23}\ cm^{-2}$  for the core-averaged column density and  $1.4 \times 10^5 - 1.7 \times 10^7\ cm^{-3}$  for

**Table 3**  
Median and Mean Values of the Derived Line Parameters for Each Category

Name	Prestellar		Protostellar								All	
	Median	Mean	Outflow Core		Warm Core		Outflow + Warm Core		Sum		Median	Mean
			Median	Mean	Median	Mean	Median	Mean	Median	Mean		
$I_{C^{18}O}$	0.98	1.12	0.81	0.88	0.86	0.96	1.22	1.30	0.90	1.09	0.93	1.11
$\sigma_{C^{18}O}$	0.75	0.89	0.88	0.95	0.92	1.02	0.85	0.97	0.88	0.99	0.79	0.92
$I_{N_2D^+}$	0.41	0.42	0.29	0.31	0.52	0.47	0.44	0.53	0.40	0.47	0.41	0.45
$\sigma_{N_2D^+}$	0.22	0.21	0.21	0.25	0.19	0.21	0.24	0.26	0.23	0.25	0.22	0.23
$I_{DCO^+}$	0.32	0.37	0.37	0.46	0.33	0.37	0.36	0.37	0.35	0.39	0.33	0.38
$\sigma_{DCO^+}$	0.29	0.30	0.29	0.29	0.38	0.39	0.32	0.35	0.32	0.35	0.30	0.32
$\sigma_{CH_3OH}$	...	...	...	...	1.23	1.59	1.46	1.98	1.35	1.82	1.35	1.82
$I_{H_2CO}$	0.18	0.19	0.28	0.28	0.33	0.42	0.61	0.88	0.38	0.60	0.26	0.41
$\sigma_{H_2CO}$	0.72	0.84	0.96	1.06	1.19	1.36	1.85	2.21	1.33	1.68	1.00	1.29
$I_{^{13}CS}$	0.38	0.38	0.27	0.27	...	...	0.18	0.18	0.22	0.22	0.28	0.30
$\sigma_{^{13}CS}$	0.34	0.34	0.46	0.46	...	...	1.30	1.30	0.88	0.88	0.42	0.61
$I_{DCN}$	...	...	...	...	...	...	0.26	0.22	0.26	0.22	0.26	0.22
$\sigma_{DCN}$	...	...	...	...	...	...	1.21	1.04	1.21	1.04	1.21	1.04
$I_{C_2D}$	0.22	0.24	...	...	...	...	...	...	...	...	0.22	0.24
$\sigma_{C_2D}$	0.13	0.17	...	...	...	...	...	...	...	...	0.13	0.17

**Note.** The units are K and  $\text{km s}^{-1}$  for peak intensity and observed line width, respectively.

the core-averaged volume density. The protostellar cores have higher column densities and volume densities than the prestellar cores (Table 4).

Assuming LTE and optically thin molecular emission, the molecular column density ( $N_{\text{mol}}$ ) can be estimated from the velocity-integrated intensity (see Appendix C for a detailed derivation of the column density). To study the properties of the molecules, we also calculated the molecular abundances,  $X_{\text{mol}} = N_{\text{mol}}/N_{\text{H}_2}$ , using the updated  $\text{H}_2$  column density and the derived molecular column densities.

The derived  $\text{N}_2\text{D}^+$  column densities range from  $5.9 \times 10^{10}$  to  $1.3 \times 10^{12} \text{ cm}^{-2}$ , resulting in  $\text{N}_2\text{D}^+$  abundances of  $2.2 \times 10^{-12}$ – $1.7 \times 10^{-11}$ . The  $\text{N}_2\text{D}^+$  column densities are similar to the value of  $6.2 \times 10^{11} \text{ cm}^{-2}$  obtained for other IRDCs (e.g., Chen et al. 2010; Germer et al. 2015; Barnes et al. 2016), and the  $\text{N}_2\text{D}^+$  abundances are comparable to the values of  $\sim 10^{-12}$  in other massive clumps (Giannetti et al. 2019). The estimated  $\text{DCO}^+$  column densities are between  $4.7 \times 10^{10}$  and  $6.5 \times 10^{11} \text{ cm}^{-2}$ , leading to  $\text{DCO}^+$  abundances of  $1.3 \times 10^{-12}$ – $2.4 \times 10^{-11}$ .  $N_{\text{DCO}^+}$  is similar to the values reported in other IRDCs ( $\leq 3 \times 10^{11} \text{ cm}^{-2}$ ; Germer et al. 2015). The derived DCN column densities and abundances are  $2.7 \times 10^{11}$ – $2.0 \times 10^{12} \text{ cm}^{-2}$  and  $5.6 \times 10^{-12}$ – $1.2 \times 10^{-11}$ , respectively. The DCN abundances are significantly lower than those in more evolved dense cores in W3 ( $> 10^{-10}$ ; Mottram et al. 2020).  $\text{C}_2\text{D}$  has column densities of  $4.8 \times 10^{12}$ – $1.1 \times 10^{13} \text{ cm}^{-2}$  and abundances of  $1.5 \times 10^{-10}$ – $4.2 \times 10^{-10}$ .

Given that these dense cores are still in very early evolutionary phases and are characterized by a cold environment,  $\text{H}_2\text{CO}$  is expected to form in ice on the grain surface and to subsequently be released to the gas phase (Jørgensen et al. 2005). We assumed an ortho-to-para ratio of 1.6, which is consistent with thermalization at a low temperature of  $T \sim 15 \text{ K}$  (Jørgensen et al. 2005). The derived  $\text{H}_2\text{CO}$  column densities and abundances are  $4.1 \times 10^{11}$ – $9.3 \times 10^{13} \text{ cm}^{-2}$  and  $1.2 \times 10^{-11}$ – $1.1 \times 10^{-9}$ , respectively.

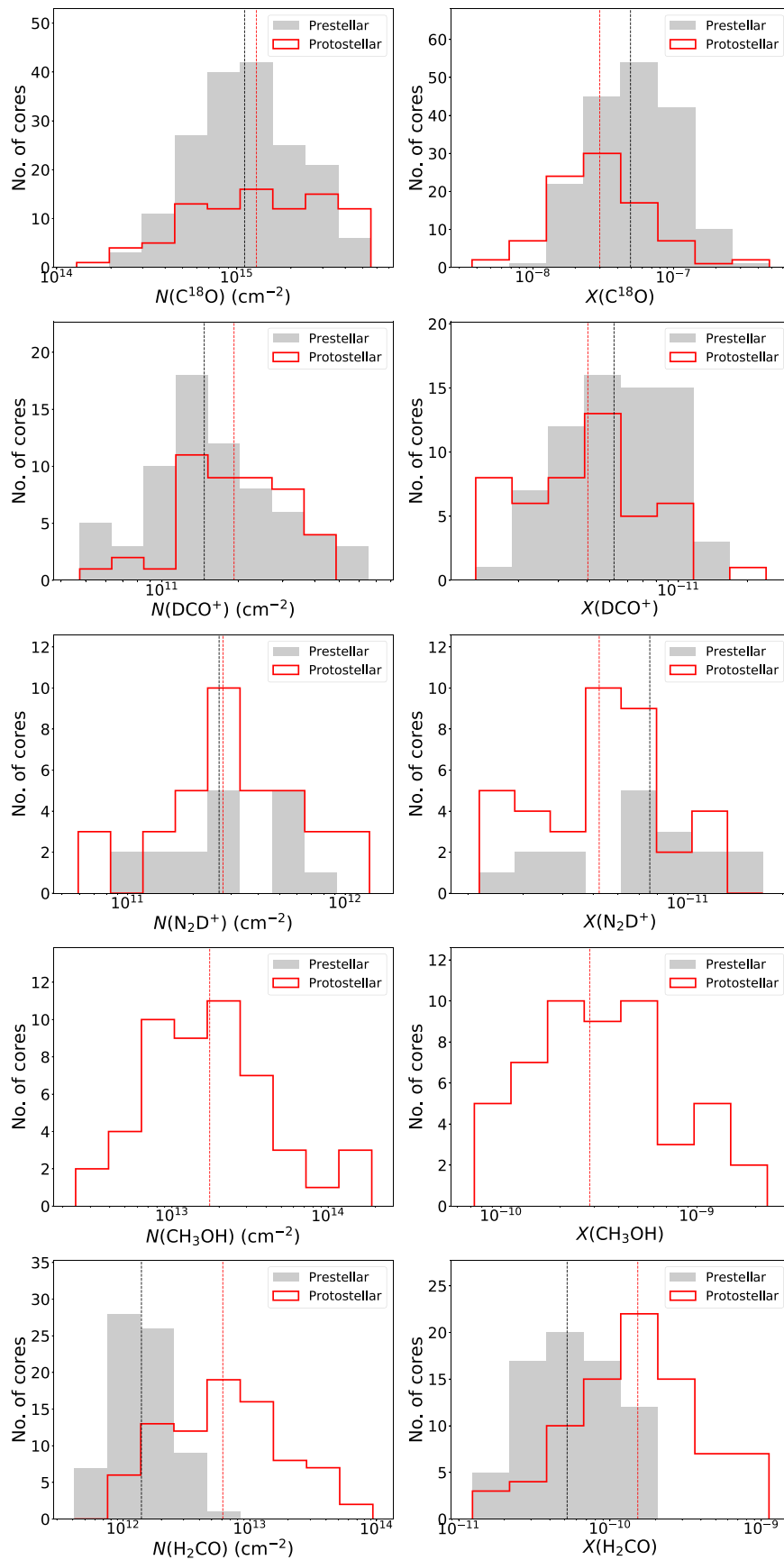
$\text{CH}_3\text{OH}$  has column densities of  $2.4 \times 10^{12}$ – $1.9 \times 10^{14} \text{ cm}^{-2}$  and abundances of  $7.3 \times 10^{-11}$ – $2.3 \times 10^{-9}$  for the detected dense cores. The abundances of  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  are similar to those in dense cores prior to the hot-core phase in other IRDCs (a few  $10^{-10}$  for  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$ ; Germer et al. 2014; Mottram et al. 2020), but lower than those in hot-core and UCHII regions ( $\geq 10^{-9}$ ; e.g., Germer et al. 2014; Mottram et al. 2020).

A  $\text{C}^{18}\text{O}$  optical correction factor,  $C_\tau = \tau_{\text{C}^{18}\text{O}}/[1 - \exp(-\tau_{\text{C}^{18}\text{O}})]$ , is applied in the calculation of the  $\text{C}^{18}\text{O}$  column density.  $C_\tau$  is derived following the approach described in Sabatini et al. (2019). The detailed estimation of the  $\text{C}^{18}\text{O}$  correction factor is presented in Sabatini et al. (2022). The calculated  $\text{C}^{18}\text{O}$  column densities vary from  $1.3 \times 10^{14}$  to  $5.6 \times 10^{15} \text{ cm}^{-2}$ , resulting in  $\text{C}^{18}\text{O}$  abundances of  $3.7 \times 10^{-9}$ – $4.8 \times 10^{-7}$ . The estimated SiO column densities vary from  $2.3 \times 10^{11}$ – $3.2 \times 10^{13} \text{ cm}^{-2}$ , which are comparable to the values in the outflows, whereas the derived abundances of  $3.0 \times 10^{-12}$ – $3.4 \times 10^{-10}$  are lower than those found in the outflows ( $\geq 1.1 \times 10^{-9}$ ; see Paper II).

Figure 5 shows histograms of the molecular column densities and abundance ratio distributions for the prestellar and protostellar cores (see also Table 4). Except for  $\text{C}^{18}\text{O}$  and  $\text{N}_2\text{D}^+$ , which have similar column densities in the prestellar and protostellar cores, all other molecules have column densities in the prestellar cores that are relatively lower than those in the protostellar cores. On the other hand, the  $\text{N}_2\text{D}^+$ ,  $\text{DCO}^+$ , and  $\text{C}^{18}\text{O}$  abundances are higher in the prestellar cores than in the protostellar cores, indicating that the abundances of these molecules tend to decrease with the evolution of the dense cores. These abundance variations are dominated by the effect of the rapid  $\text{H}_2$  density increase from the prestellar to protostellar phases (see Section 4.2). In contrast, the abundance of  $\text{H}_2\text{CO}$  in the protostellar cores is higher than in the prestellar ones, suggesting that its abundance can be enhanced with core evolution.

**Table 4**  
Median and Mean values of the Derived Core Properties for Each Category

Name	Prestellar		Protostellar								All	
	Median	Mean	Outflow Core		Warm Core		Outflow + Warm Core		Sum		Median	Mean
$T_{\text{NH}_3}(\text{K})$	14.1	14.2	12.8	13.8	14.8	14.3	15.3	14.9	14.8	14.4	14.4	14.3
Core-averaged volume densities ( $\text{cm}^{-3}$ ) and averaged column densities ( $\text{cm}^{-2}$ )												
$n_{\text{H}_2}$	1.06E+06	1.51E+06	1.52E+06	2.50E+06	1.20E+06	2.69E+06	3.42E+06	5.28E+06	2.30E+06	3.69E+06	1.25E+06	2.23E+06
$N_{\text{H}_2}$	2.10E+22	2.56E+22	3.25E+22	3.83E+22	2.57E+22	4.15E+22	5.64E+22	7.91E+22	4.36E+22	5.59E+22	2.56E+22	3.56E+22
Column Densities ( $\text{cm}^{-2}$ )												
$N_{\text{C}^{18}\text{O}}$	1.10E+15	1.42E+15	8.35E+14	1.30E+15	1.18E+15	1.54E+15	1.79E+15	2.20E+15	1.29E+15	1.77E+15	1.16E+15	1.54E+15
$N_{\text{N}_2\text{D}^+}$	2.63E+11	3.30E+11	2.28E+11	2.61E+11	3.55E+11	4.06E+11	2.96E+11	4.39E+11	2.74E+11	3.94E+11	2.72E+11	3.74E+11
$N_{\text{DCO}^+}$	1.47E+11	1.89E+11	1.71E+11	2.12E+11	2.22E+11	2.37E+11	1.92E+11	2.05E+11	1.92E+11	2.18E+11	1.67E+11	2.01E+11
$N_{\text{CH}_3\text{OH}}$	...	...	...	...	8.36E+12	2.09E+13	1.86E+13	3.61E+13	1.74E+13	2.98E+13	1.74E+13	2.98E+13
$N_{\text{H}_2\text{CO}}$	1.39E+12	1.61E+12	2.84E+12	3.00E+12	4.29E+12	5.83E+12	1.20E+13	2.04E+13	6.11E+12	1.18E+13	2.43E+12	7.09E+12
$N_{^{13}\text{CS}}$	1.14E+12	1.14E+12	1.06E+12	1.06E+12	...	...	1.89E+12	1.89E+12	1.47E+12	1.47E+12	1.29E+12	1.31E+12
$N_{\text{DCN}}$	...	...	...	...	...	...	7.73E+11	1.05E+12	7.73E+11	1.05E+12	7.73E+11	1.05E+12
$N_{\text{C}_2\text{D}}$	8.91E+12	8.33E+12	...	...	...	...	...	...	...	...	8.91E+12	8.33E+12
$N_{\text{SiO}}$	...	...	1.74E+12	1.46E+12	...	...	1.70E+12	5.59E+12	1.74E+12	5.13E+12	1.74E+12	5.13E+12
Molecular Abundances												
$X_{\text{C}^{18}\text{O}}$	4.95E-08	6.74E-08	3.53E-08	3.68E-08	3.85E-08	6.37E-08	2.33E-08	2.95E-08	2.99E-08	4.43E-08	4.23E-08	5.96E-08
$X_{\text{N}_2\text{D}^+}$	7.57E-12	8.07E-12	5.94E-12	5.99E-12	7.78E-12	7.91E-12	4.90E-12	5.07E-12	5.23E-12	5.81E-12	6.12E-12	6.52E-12
$X_{\text{DCO}^+}$	5.23E-12	5.95E-12	4.79E-12	4.71E-12	6.58E-12	7.60E-12	2.46E-12	2.84E-12	4.02E-12	4.98E-12	4.78E-12	5.56E-12
$X_{\text{CH}_3\text{OH}}$	...	...	...	...	2.75E-10	4.44E-10	3.00E-10	4.72E-10	2.83E-10	4.60E-10	2.83E-10	4.60E-10
$X_{\text{H}_2\text{CO}}$	5.20E-11	6.88E-11	8.09E-11	8.74E-11	1.59E-10	2.40E-10	1.76E-10	2.80E-10	1.53E-10	2.32E-10	8.87E-11	1.57E-10
$X_{^{13}\text{CS}}$	6.03E-11	6.03E-11	7.94E-11	7.94E-11	...	...	1.52E-11	1.52E-11	4.73E-11	4.73E-11	5.41E-11	5.38E-11
$X_{\text{DCN}}$	...	...	...	...	...	...	8.30E-12	8.55E-12	8.30E-12	8.55E-12	8.30E-12	8.55E-12
$X_{\text{C}_2\text{D}}$	1.79E-10	2.50E-10	...	...	...	...	...	...	...	...	1.79E-10	2.50E-10
$X_{\text{SiO}}$	...	...	4.05E-11	4.38E-11	...	...	3.26E-11	5.69E-11	3.35E-11	5.54E-11	3.35E-11	5.54E-11



**Figure 5.** Left column: histograms of the molecular column densities for the prestellar and protostellar cores. The black dashed vertical lines indicate the median values of the parameters. Right column: histograms of the molecular abundances for the prestellar and protostellar cores.

## 4. Discussion

### 4.1. Missing Flux

To understand the impact of the missing flux on the line emission, we compared the 12m7m and 12m7mTP data sets. We investigated the integrated intensities, peak intensities, line widths, and central velocities of the line emissions between the two data sets.

For the  $\text{N}_2\text{D}^+$  line emission, we find that the 12m7m data have recovered about 92% of the 12m7mTP flux. The differences of the measured  $I$  and  $\sigma_{\text{obs}}$  are factors of 0.94 and 0.99, respectively. For the  $\text{DCO}^+$  line emission, the mean ratios of 12m7m to 12m7mTP are 0.89 for  $I$  and 0.9 for  $\sigma_{\text{obs}}$ , resulting a mean flux ratio (velocity-integrated intensity) of 0.79. The  $\text{DCO}^+$  emission behavior is very similar to that of  $\text{N}_2\text{D}^+$ . These results indicate that most of the  $\text{N}_2\text{D}^+$  and  $\text{DCO}^+$  emission is compact and recovered without the addition of TP data from single-dish telescopes.

For the  $\text{H}_2\text{CO}$  ( $3_{0,3} - 2_{0,2}$ ) line emission, the 12m7m data recover about 71% of the 12m7mTP flux, and the mean ratios of 12m7m to 12m7mTP for  $I$  and  $\sigma_{\text{obs}}$  are 0.82 and 0.87, respectively. On the other hand,  $\text{CH}_3\text{OH}$  has similar flux,  $I$ , and  $\sigma_{\text{obs}}$  between the 12m7m and 12m7mTP data sets; the mean ratio (12m7m/12m7mTP) is 0.94 for flux, 0.94 for  $I$ , and 1.0 for  $\sigma_{\text{obs}}$ . This indicates that  $\text{CH}_3\text{OH}$  traces more spatially compact emission compared with  $\text{H}_2\text{CO}$ . This suggests that the observed  $\text{CH}_3\text{OH}$  transition may preferentially be concentrated near the protostars or in knots in outflows.

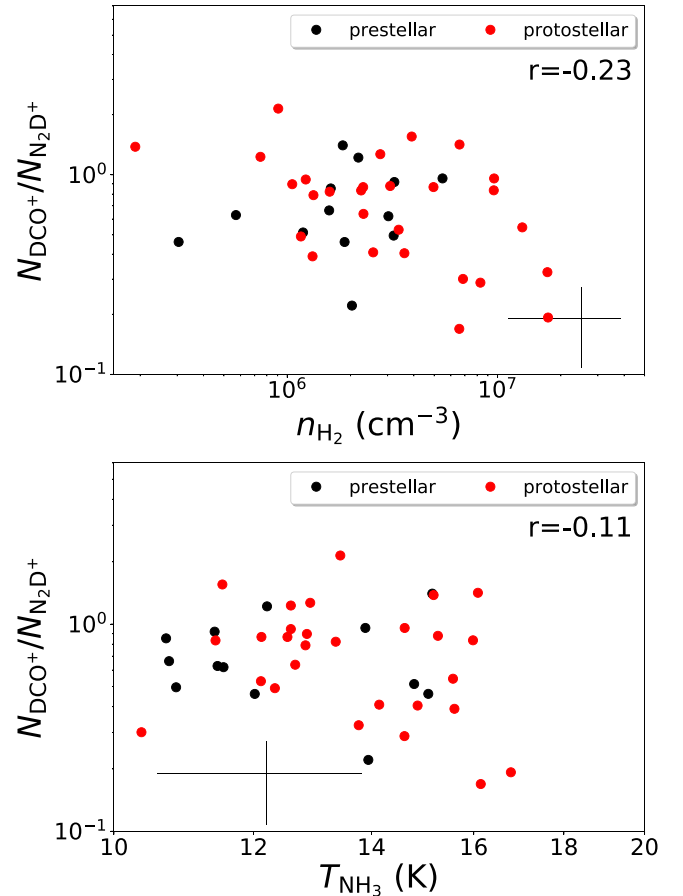
For  $\text{C}^{18}\text{O}$ , the mean ratios of the 12m7m to 12m7mTP data are 0.54 for the intensity peak and 0.7 for the velocity dispersion, resulting in a mean flux ratio of 0.36. Among the detected lines (excluding CO),  $\text{C}^{18}\text{O}$  suffers most severely from missing flux. This indicates that  $\text{C}^{18}\text{O}$  probes a significant amount of diffuse molecular gas. For the remaining lines with relatively low detection rates, their 12m7m images are weakly affected by the missing flux. The mean flux ratios of 12m7m to 12m7mTP are 1.0 for SiO, 0.96 for  $^{13}\text{CS}$ , 0.9 for DCN, and 0.98 for  $\text{C}_2\text{D}$ .

### 4.2. Deuterated Molecules

$\text{N}_2\text{D}^+$  is expected to be abundant in cold ( $<20$  K) and dense ( $\sim 10^5 \text{ cm}^{-3}$ ) regions, in which its major destroyer, CO, is significantly depleted onto grain surfaces.  $\text{N}_2\text{D}^+$  can be formed via  $\text{N}_2$  reacting with  $\text{H}_2\text{D}^+$  (dominant reaction:  $\text{N}_2 + \text{H}_2\text{D}^+ \rightarrow \text{N}_2\text{D}^+ + \text{H}_2$ ),  $\text{D}_2\text{H}^+$ , or  $\text{D}_3^+$  (Pagani et al. 2009), and destroyed by CO ( $\text{N}_2\text{D}^+ + \text{CO} \rightarrow \text{DCO}^+ + \text{N}_2$ ) or electrons ( $\text{N}_2\text{D}^+ + e^- \rightarrow \text{ND} + \text{N}$  or  $\text{D} + \text{N}_2$ ; Sakai et al. 2022).  $\text{DCO}^+$  is also considered to be a cold and dense gas tracer. However,  $\text{DCO}^+$  requires gas-phase CO for its formation at cold temperatures ( $T < 20\text{--}50$  K), i.e.,  $\text{H}_2\text{D}^+ + \text{CO} \rightarrow \text{DCO}^+ + \text{H}_2$  (Wootten & Loren 1987). Therefore, the  $\text{DCO}^+$  abundance does not decrease rapidly when CO is released to the gas phase from the grain mantles (Dalgarno & Lepp 1984). The different chemistry between  $\text{N}_2\text{D}^+$  and  $\text{DCO}^+$  may explain their different spatial distributions as seen in Figure 1 (e.g., Sakai et al. 2022). DCN and  $\text{C}_2\text{D}$  tend to form in warm environments (Turner 2001; Albertsson et al. 2013).

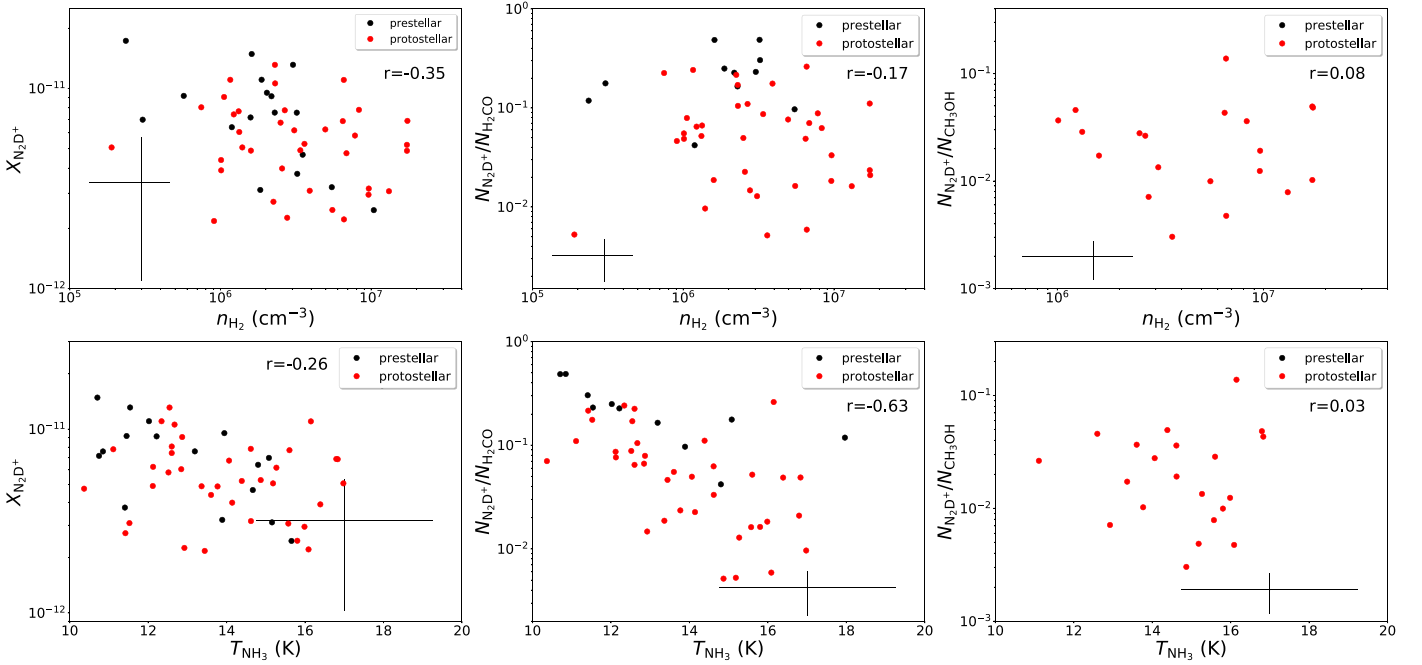
The  $\text{N}_2\text{D}^+$  and  $\text{DCO}^+$  column densities exhibit a strong correlation (see Figure 15 in Appendix A), with a Spearman rank correlation coefficient<sup>17</sup> of  $r = 0.58$ . This is mostly

<sup>17</sup> Spearman's rank correlation test is a nonparametric measure of the monotonicity of the relationship between two variables. A correlation coefficient  $|r| \geq 0.5$  means strong correlation,  $0.5 > |r| \geq 0.3$  means moderate correlation,  $0.3 > |r| \geq 0.1$  means weak correlation, and  $0.1 > |r|$  means no correlation (Cohen 1988).

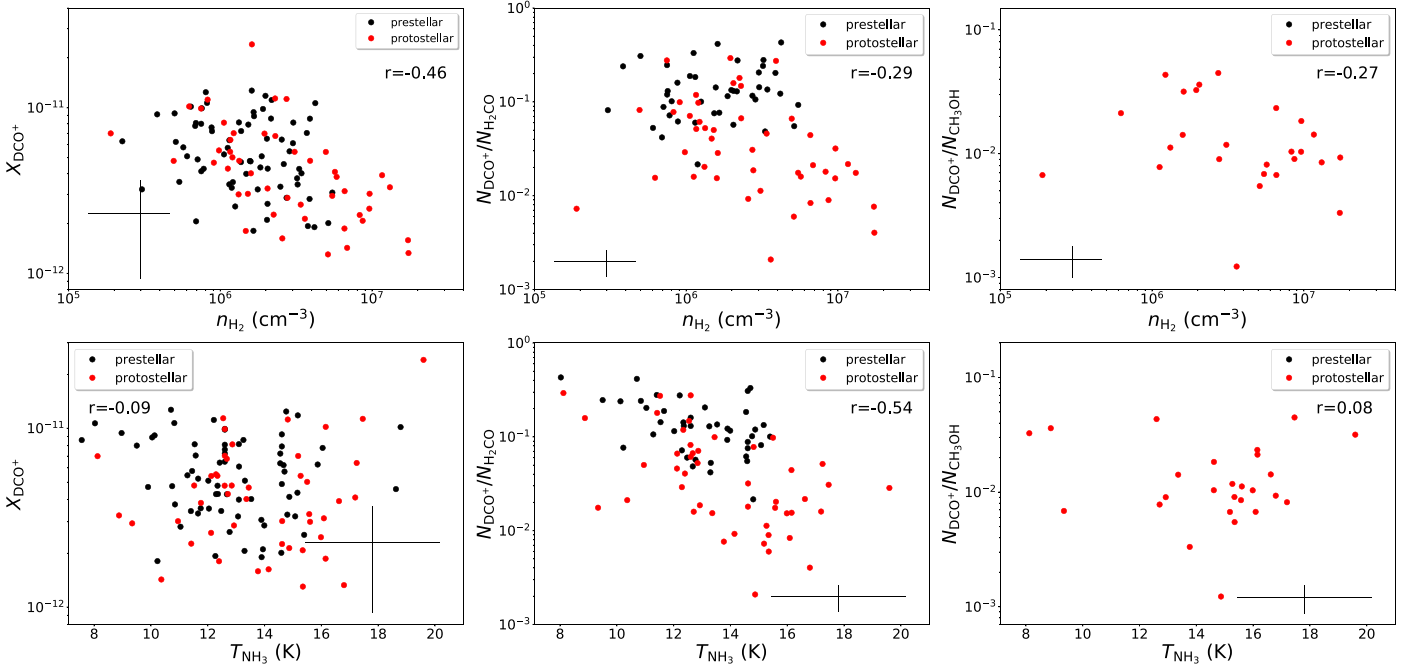


**Figure 6.** The column density ratio of  $\text{DCO}^+$  to  $\text{N}_2\text{D}^+$  vs. the core-averaged volume density  $n_{\text{H}_2}$  and temperature  $T_{\text{NH}_3}$ .

because both lines trace cold and dense gas in the dense cores. The  $\text{N}_2\text{D}^+$  abundance appears to decrease with increasing volume densities  $n_{\text{H}_2}$ , with a moderate correlation coefficient of  $-0.35$  (see Figure 7). As mentioned in Section 3.4, the volume density increases with the evolution of the dense cores, which continue to accumulate mass via the accretion of material from natal clumps. The  $n_{\text{H}_2}\text{--}X_{\text{N}_2\text{D}^+}$  anticorrelation suggests that the  $\text{N}_2\text{D}^+$  abundance decreases with core evolution. As the cores evolve, the gas temperature increases, thereby lowering the deuterium enhancement. In this case, one naively expects an anticorrelation between the  $\text{N}_2\text{D}^+$  abundance and  $T_{\text{NH}_3}$ . As seen in Figure 7, there is no obvious trend between the  $\text{N}_2\text{D}^+$  abundance and  $T_{\text{NH}_3}$ . These cores are still very cold, with temperatures between 10 and 20 K, which are lower than the sublimation temperature of CO ( $\sim 25$  K). This may explain why the  $\text{N}_2\text{D}^+$  abundance does not vary significantly with  $T_{\text{NH}_3}$ . In addition, this suggests that these cores are still at a very early evolutionary phase, in which the surrounding environment has not been significantly warmed up by young stellar objects. On the other hand, we cannot completely rule out the possibility that  $T_{\text{NH}_3}$  does not accurately reflect the true temperature of the dense molecular gas traced by  $\text{N}_2\text{D}^+$ , because the spatial resolution of  $T_{\text{NH}_3}$  ( $\sim 5''$ ) is coarser than the ALMA observations ( $\sim 1''$ ) and the critical density of  $\text{NH}_3$  (1,1) is only of a few  $10^4 \text{ cm}^{-3}$ . Determinations of temperatures at  $\sim 1''$  scales would be necessary to verify whether the  $T_{\text{NH}_3}$  varies significantly down to the small scale. The  $n_{\text{H}_2}\text{--}X_{\text{N}_2\text{D}^+}$  and  $X_{\text{N}_2\text{D}^+}\text{--}T_{\text{NH}_3}$  results



**Figure 7.** Top row: plots of  $N_{\text{H}_2}$  vs.  $N_{\text{N}_2\text{D}^+}$ ,  $N_{\text{N}_2\text{D}^+}/N_{\text{H}_2\text{CO}}$ , and  $N_{\text{N}_2\text{D}^+}/N_{\text{CH}_3\text{OH}}$ . Bottom row: plots of  $T_{\text{NH}_3}$  vs.  $X_{\text{N}_2\text{D}^+}$ ,  $N_{\text{N}_2\text{D}^+}/N_{\text{H}_2\text{CO}}$ , and  $N_{\text{N}_2\text{D}^+}/N_{\text{CH}_3\text{OH}}$ . The correlation coefficients derived from Spearman’s rank correlation test are given in the text inside each panel. The black cross shows the typical uncertainty in each panel.



**Figure 8.** The same as Figure 7, but for  $\text{DCO}^+$ .

suggest that the  $\text{N}_2\text{D}^+$  abundance variation is dominated by the  $\text{H}_2$  core density in the ASHES sample.

The column density ratio of  $N_{\text{N}_2\text{D}^+}/N_{\text{H}_2\text{CO}}$  appears to decrease as a function of increasing  $n_{\text{H}_2}$ . However, a closer look reveals that this weak anticorrelation is mostly dominated by the protostellar cores. Both  $N_{\text{N}_2\text{D}^+}$  and  $N_{\text{H}_2\text{CO}}$  tend to increase with  $n_{\text{H}_2}$ , and therefore the  $N_{\text{N}_2\text{D}^+}/N_{\text{H}_2\text{CO}}-n_{\text{H}_2}$  anticorrelation implies that  $N_{\text{H}_2\text{CO}}$  is more sensitive to  $n_{\text{H}_2}$  than  $N_{\text{N}_2\text{D}^+}$  toward the protostellar cores (see also Section 3.3). In addition, the  $N_{\text{N}_2\text{D}^+}/N_{\text{H}_2\text{CO}}$  ratio also appears to decrease with increasing

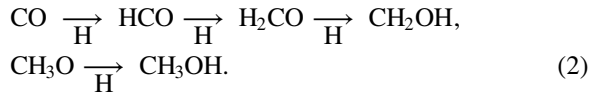
$T_{\text{NH}_3}$ , with a correlation coefficient of  $-0.63$ . This is because the  $\text{H}_2\text{CO}$  abundance is enhanced by elevated temperatures. The  $N_{\text{N}_2\text{D}^+}/N_{\text{CH}_3\text{OH}}$  ratio shows no clear trend with  $n_{\text{H}_2}$  or  $T_{\text{NH}_3}$ . In general,  $\text{DCO}^+$  shows a similar trend to those seen in  $\text{N}_2\text{D}^+$ , except for  $n_{\text{H}_2}-N_{\text{DCO}^+}/N_{\text{CH}_3\text{OH}}$  ( $r = -0.27$ ), which presents a weak anticorrelation. The difference in  $\text{N}_2\text{D}^+$  and  $\text{DCO}^+$  may be a result of different chemistry.

There is a weak anticorrelation between  $n_{\text{H}_2}$  and the  $N_{\text{DCO}^+}/N_{\text{N}_2\text{D}^+}$  ratio (see Figure 6), with a correlation coefficient of  $r = -0.23$ . From Figures 7 and 8, one notes

that both the  $\text{N}_2\text{D}^+$  and  $\text{DCO}^+$  abundances decrease with increasing  $n_{\text{H}_2}$ , thereby causing the ratio of  $\text{DCO}^+$  to  $\text{N}_2\text{D}^+$  to change slightly with  $n_{\text{H}_2}$ . In addition, the  $N_{\text{DCO}^+}/N_{\text{N}_2\text{D}^+}$  ratio shows only minor changes with  $T_{\text{NH}_3}$ , which gives a correlation coefficient of  $r = -0.11$ . This can be ascribed to the fact that the both  $\text{DCO}^+$  and  $\text{N}_2\text{D}^+$  abundances do not vary significantly with  $T_{\text{NH}_3}$  (see Figures 7 and 8).

#### 4.3. $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$

$\text{CH}_3\text{OH}$  is considered to be mostly formed on the surface of dust grains, via the hydrogenation of CO with some intermediate products (e.g.,  $\text{H}_2\text{CO}$ ; Charnley et al. 1997; Watanabe et al. 2004; Fuchs et al. 2009):



Unlike  $\text{CH}_3\text{OH}$ , which forms entirely on the surfaces of dust grains,  $\text{H}_2\text{CO}$  can be formed efficiently through both grain surface reaction in cold environments and gas-phase reactions in warm/hot environments (Le Teuff et al. 2000; Garrod et al. 2006; Fuchs et al. 2009).

$\text{CH}_3\text{OH}$  shows a dip in its emission distribution at the center of some dense cores, such as the protostellar core #15 in G337.54 (Appendix A). A similar feature has been observed in low-mass prestellar cores, e.g., L1498 and L1517B (Tafalla et al. 2006). These authors suggest that the weaker  $\text{CH}_3\text{OH}$  emission toward the center of the dense cores is due to the significant  $\text{CH}_3\text{OH}$  depletion in cold and dense environments. Therefore, the low detection rate of  $\text{CH}_3\text{OH}$  in dense cores may be partly ascribed to  $\text{CH}_3\text{OH}$  depletion.

Among the detected molecules, the  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  column densities show the strongest correlation, with correlation coefficients of 0.83 (see Figure 15 in Appendix A). As mentioned in Section 3.3, both  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  tend to probe dense and high-velocity molecular gas, and hence the protostellar activity may be partly responsible for the strong correlation of the two species. For example, outflows/shocks can release both  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  from grain mantles to the gas phase. In addition, both the  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  column densities show strong correlations with the SiO column density (see Figure 15 in Appendix A); the correlation coefficient is 0.73 for  $N_{\text{H}_2\text{CO}}-N_{\text{SiO}}$  and 0.84 for  $N_{\text{CH}_3\text{OH}}-N_{\text{SiO}}$ .

The derived abundance ratios of  $\text{H}_2\text{CO}/\text{CH}_3\text{OH} = 0.1-2.3$  are comparable to the values of 0.9–2.5 reported in dense clumps ( $n_{\text{H}_2} \sim 10^6 \text{ cm}^{-3}$ ; Leurini et al. 2010), hot corinos (0.7–4.3; Maret et al. 2004, 2005), and low-mass starless cores (1.1–2.2, e.g., L1498 and L1517B; Tafalla et al. 2006). These values are higher than the abundance ratios derived in hot cores (0.13–0.28; Bisschop et al. 2007) and the shocked gas in the Galactic Center clouds (0.01–0.1; Requena-Torres et al. 2006; Lu et al. 2021), whereas they are significantly lower than those in the interclump medium ( $\text{H}_2\text{CO}/\text{CH}_3\text{OH} = 14-1400$ ;  $n_{\text{H}_2} \sim 10^4 \text{ cm}^{-3}$ ; Leurini et al. 2010). The discrepancies could be attributed to either different dominant formation mechanisms or different chemical conditions. A detailed chemical modeling and observational comparison is needed to distinguish between these possibilities, which is beyond the scope of this paper.

## 5. Conclusion

In this paper, we analyze ALMA data from the ASHES project to investigate the chemistry of 294 dense cores in 12 massive 70  $\mu\text{m}$  dark clumps. We have studied the spatial distributions and chemical variations of  $\text{C}^{18}\text{O}$ ,  $\text{DCO}^+$ ,  $\text{N}_2\text{D}^+$ , DCN,  $\text{C}_2\text{D}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $^{13}\text{CS}$ , and SiO in different evolutionary phases of dense cores. The main results are summarized below.

1. The detection rates of the  $\text{DCO}^+$  emission in the prestellar and protostellar cores are higher than those for  $\text{N}_2\text{D}^+$ , whereas  $\text{N}_2\text{D}^+$  is more sensitive to core evolution than  $\text{DCO}^+$  in terms of clear variations of  $\sigma_{\text{obs}}$ . The commonly detected  $\text{DCO}^+$  emission toward deeply embedded dense cores suggests that it is a good tracer of prestellar (detection rate: 35%) and early-phase protostellar cores (detection rate: 49%). On the other hand, we find that  $\text{N}_2\text{D}^+$  does not exclusively trace the prestellar cores and that it is more frequently detected in the relatively earlier phase of the protostellar cores; the detection rate is 9% for the prestellar cores and 38% for the protostellar cores. This suggests that  $\text{N}_2\text{D}^+$  is not the best tracer of prestellar cores at the sensitivity obtained in ASHES.
2. Both the  $\text{N}_2\text{D}^+$  and  $\text{DCO}^+$  abundances decrease with core evolution. This is mainly caused by the effects of the  $\text{H}_2$  density increasing rapidly and the temperature increasing slowly from the prestellar to the protostellar phases in the identified cores. This can also explain why the  $\text{C}^{18}\text{O}$  abundance is higher in the prestellar cores than in the protostellar cores.
3. The detection rate of the  $\text{H}_2\text{CO}$  emission toward dense cores is 52%, three times higher than that of  $\text{CH}_3\text{OH}$  (17%). The high detection rates of  $\text{H}_2\text{CO}$  in both the prestellar (37%) and protostellar cores (87%) suggest that  $\text{H}_2\text{CO}$  is commonly seen in the very early evolutionary phase. The line widths of  $\text{H}_2\text{CO}$  are higher than those for  $\text{C}^{18}\text{O}$ ,  $\text{N}_2\text{D}^+$ , and  $\text{DCO}^+$  toward the protostellar cores, which is likely due to the fact that the  $\text{H}_2\text{CO}$  line is associated with more turbulent gas components relating to protostellar activities (e.g., outflows). The  $\text{H}_2\text{CO}$  abundances are found to increase with the evolutions of the dense cores, as well as the line intensity and line width of the  $\text{H}_2\text{CO}$  ( $3_{0,3}-2_{0,2}$ ) transition. These results indicate that  $\text{H}_2\text{CO}$  could be used as a diagnostic tool for inferring star formation activities.

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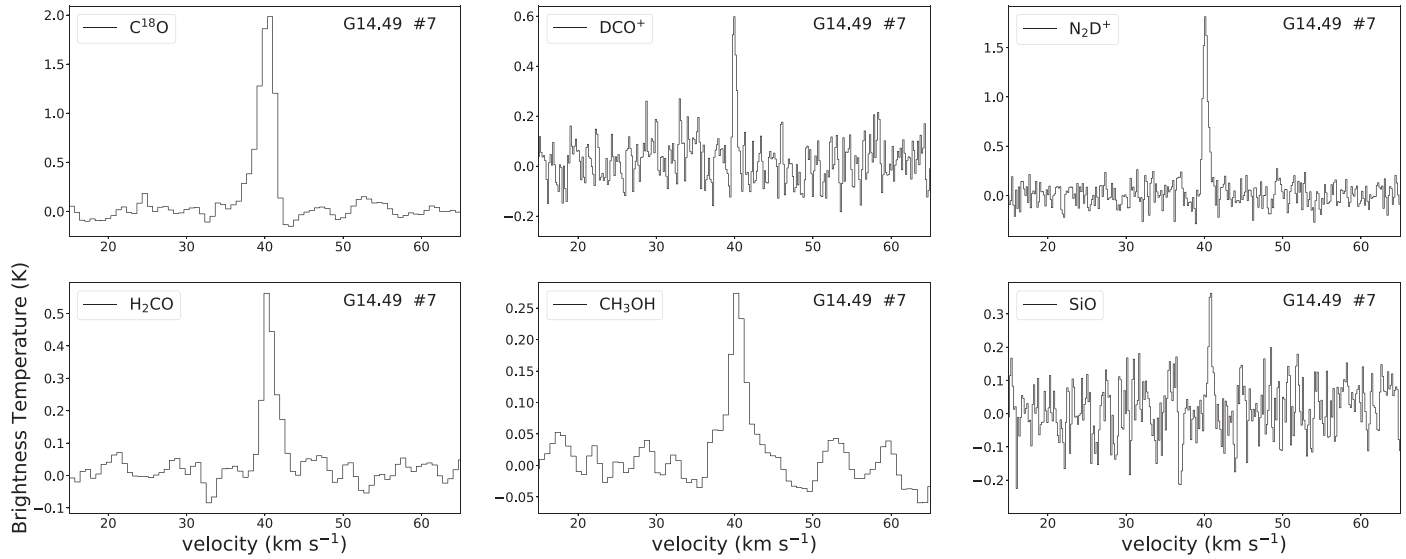
K.T. was supported by JSPS KAKENHI (grant No. 20H05645). This paper makes use of the following ALMA data: ADS/JAO. ALMA#2015.1.01539.S. ALMA is a partnership of ESO (representing its member states), NSF (USA), and NINS (Japan), together with NRC (Canada), MOST and ASIAA (Taiwan), and KASI (Republic of Korea), in cooperation with the Republic of Chile. The Joint ALMA Observatory is operated by ESO, AUI/NRAO, and NAOJ. The data analysis was partly carried out on the open use data analysis computer system at the Astronomy Data Center (ADC) of the National Astronomical Observatory of Japan.

*Facility:* ALMA.

*Software:* CASA (McMullin et al. 2007), APLpy (Robitaille & Bressert 2012), Astropy (Astropy Collaboration et al. 2013), Matplotlib (Hunter 2007), PySpecKit (Ginsburg et al. 2022).

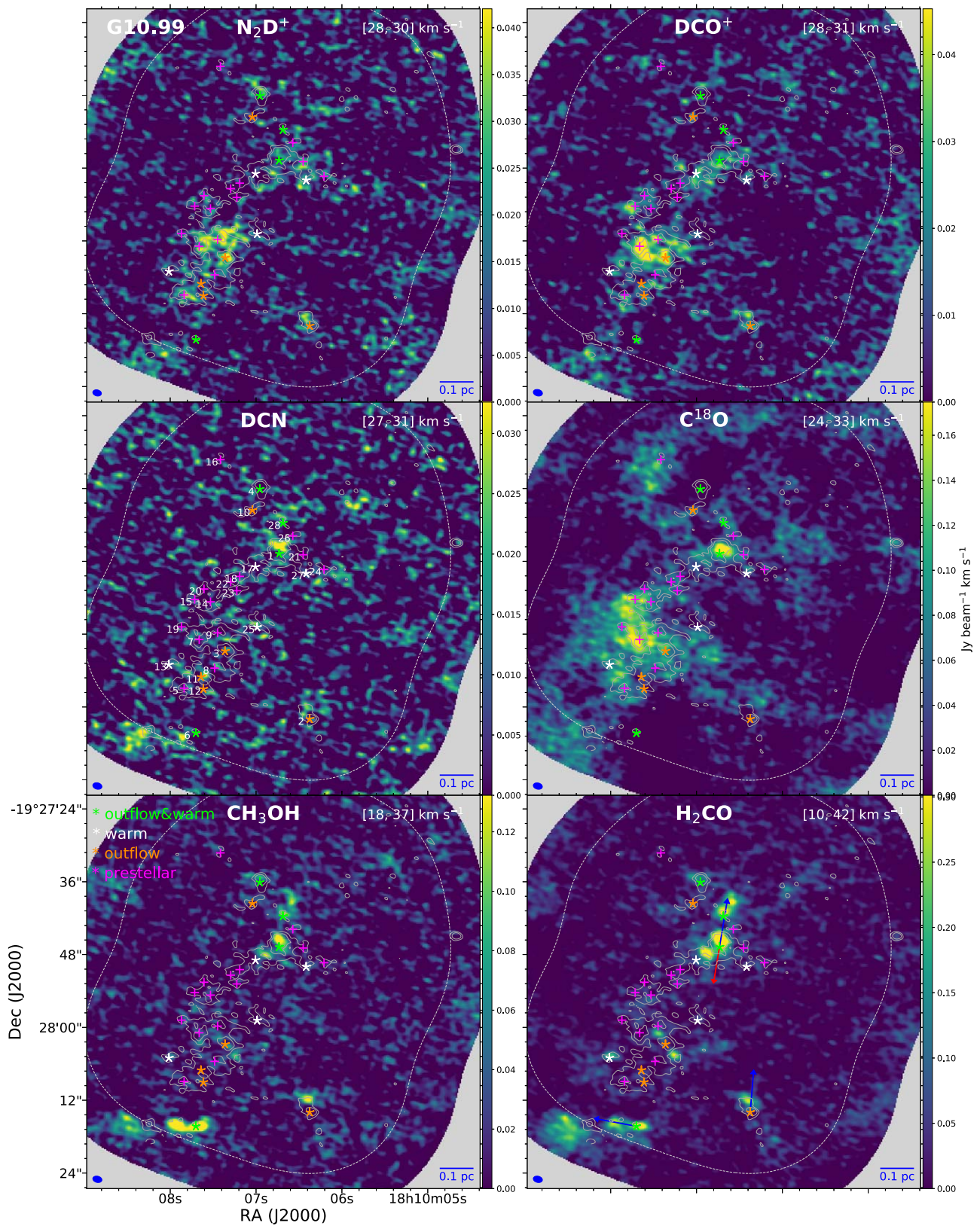
## Appendix A Additional Figures and Table

Figure 9 shows the core-averaged spectra of the detected molecular lines in G14.49 as examples. Figures 10–14 show velocity-integrated intensity maps of the  $\text{N}_2\text{D}^+$ ,  $\text{DCO}^+$ ,  $\text{DCN}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{C}^{18}\text{O}$  line emissions for each clump. Figure 15 shows the correlation of each pair of molecular column



**Figure 9.** Examples of core-averaged spectra of  $\text{C}^{18}\text{O}$ ,  $\text{DCO}^+$ ,  $\text{N}_2\text{D}^+$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{SiO}$  for core #7 in G14.49.





**Figure 10.** Velocity-integrated intensity maps of the  $\text{N}_2\text{D}^+$ ,  $\text{DCO}^+$ ,  $\text{DCN}$ ,  $\text{C}^{18}\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2\text{CO}$  emission lines toward G10.99. The fuchsia pluses and the yellow, white, and green asterisk symbols indicate prestellar candidates (category 1), outflow cores (category 2), warm cores (category 3), and outflow + warm cores (category 4). The dashed white line shows 30% of the sensitivity level of the mosaic in the ALMA continuum image. The blue and red arrows in middle right panel indicate the directions of the blueshifted and redshifted CO outflow lobes (see Paper II), respectively. The gray contours in each panel shows the 1.3 mm continuum emission. The contour levels are  $(3, 6) \times \sigma$ , with  $\sigma = 0.115 \text{ mJy beam}^{-1}$ . The beam size is shown in the lower left corner of each panel.

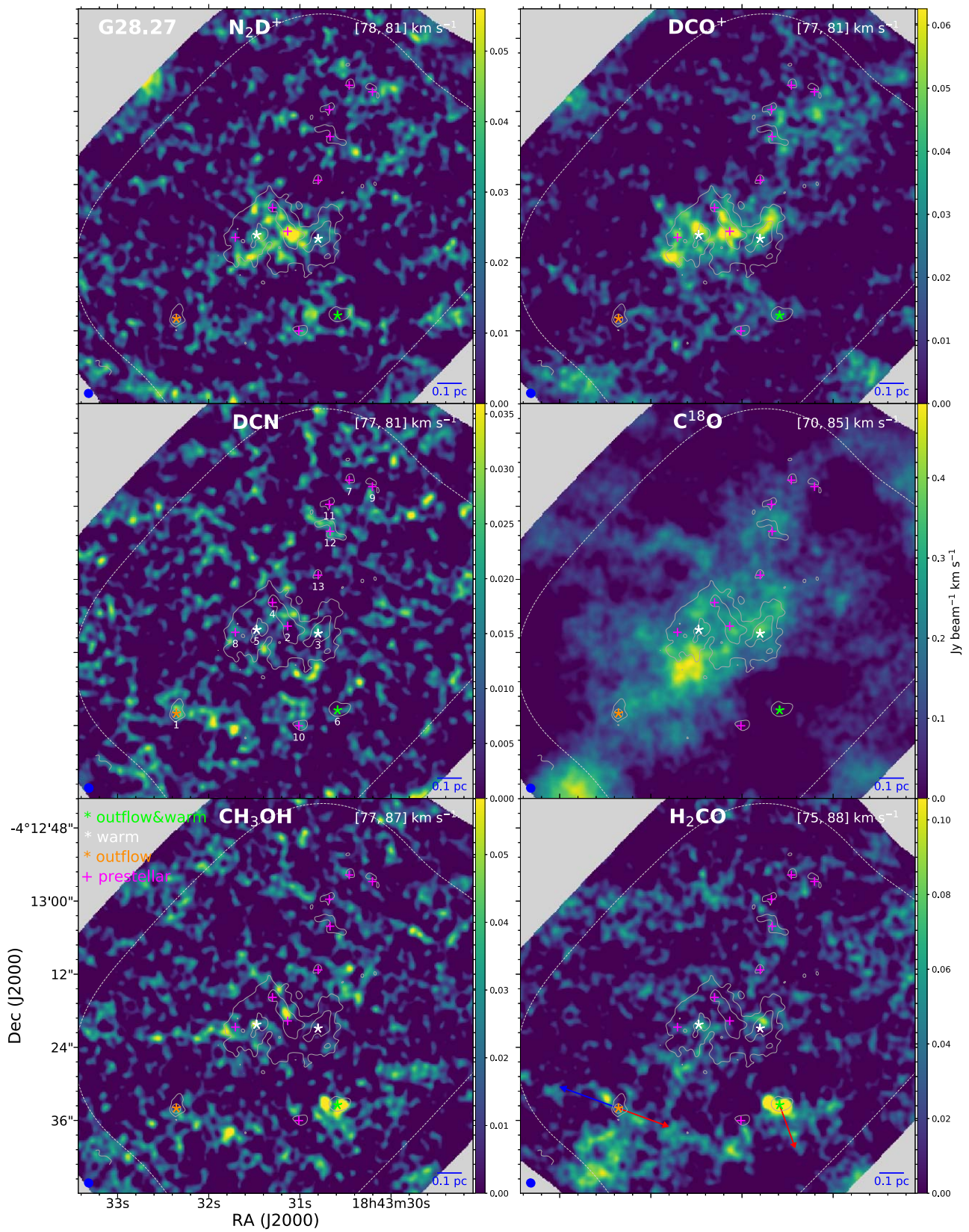


Figure 10. (Continued.)

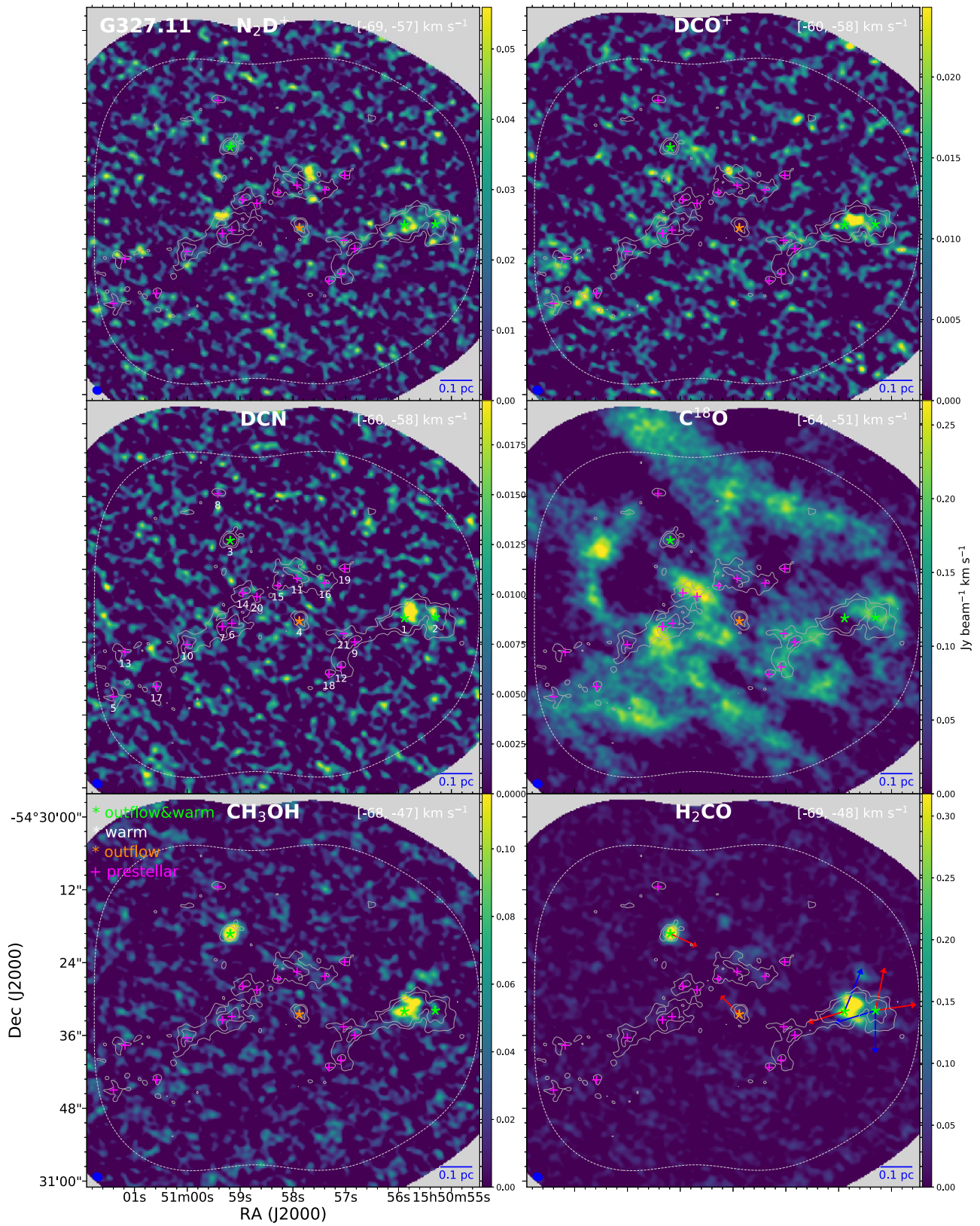


Figure 10. (Continued.)

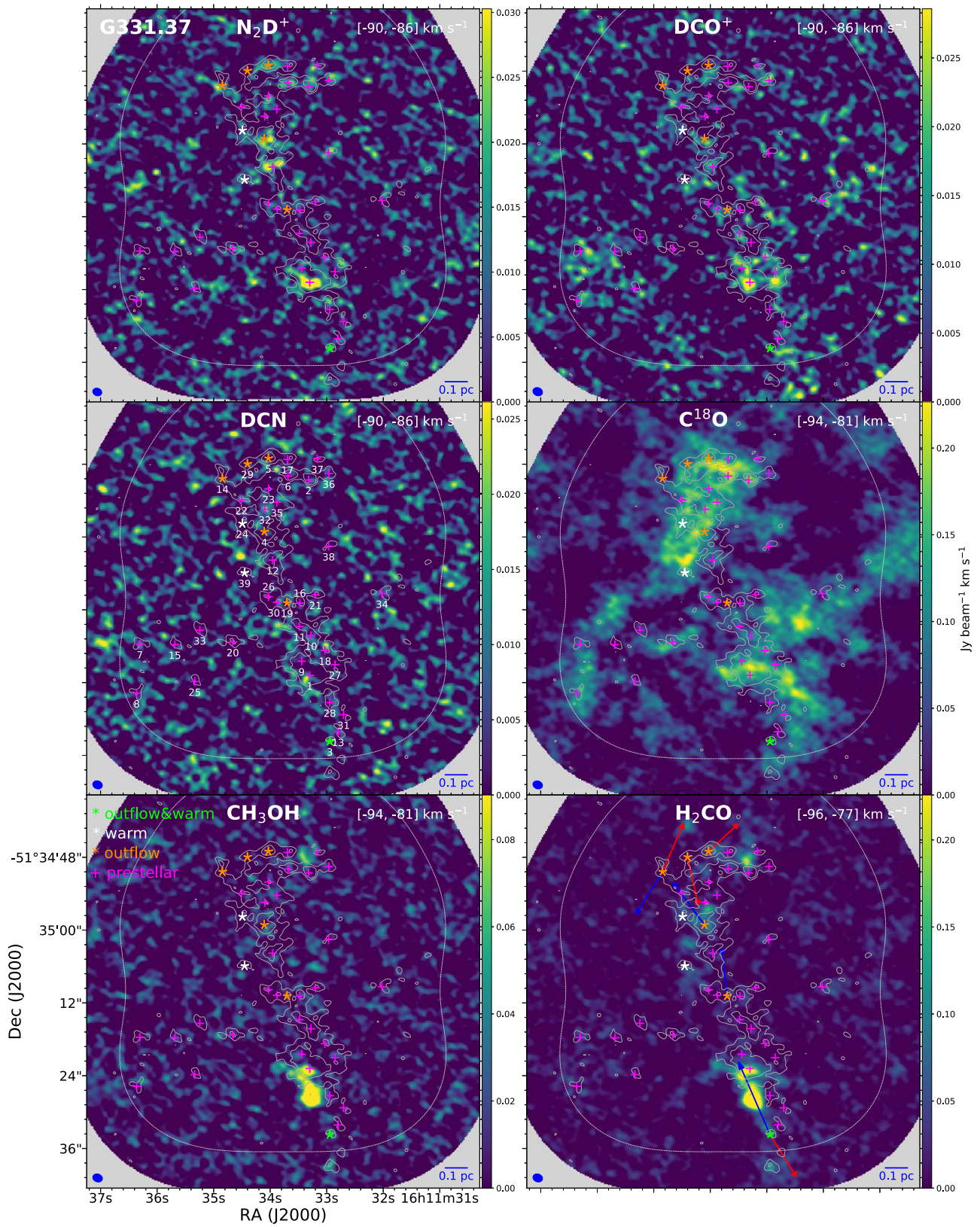


Figure 11. The same as Figure 10, but for different sources.

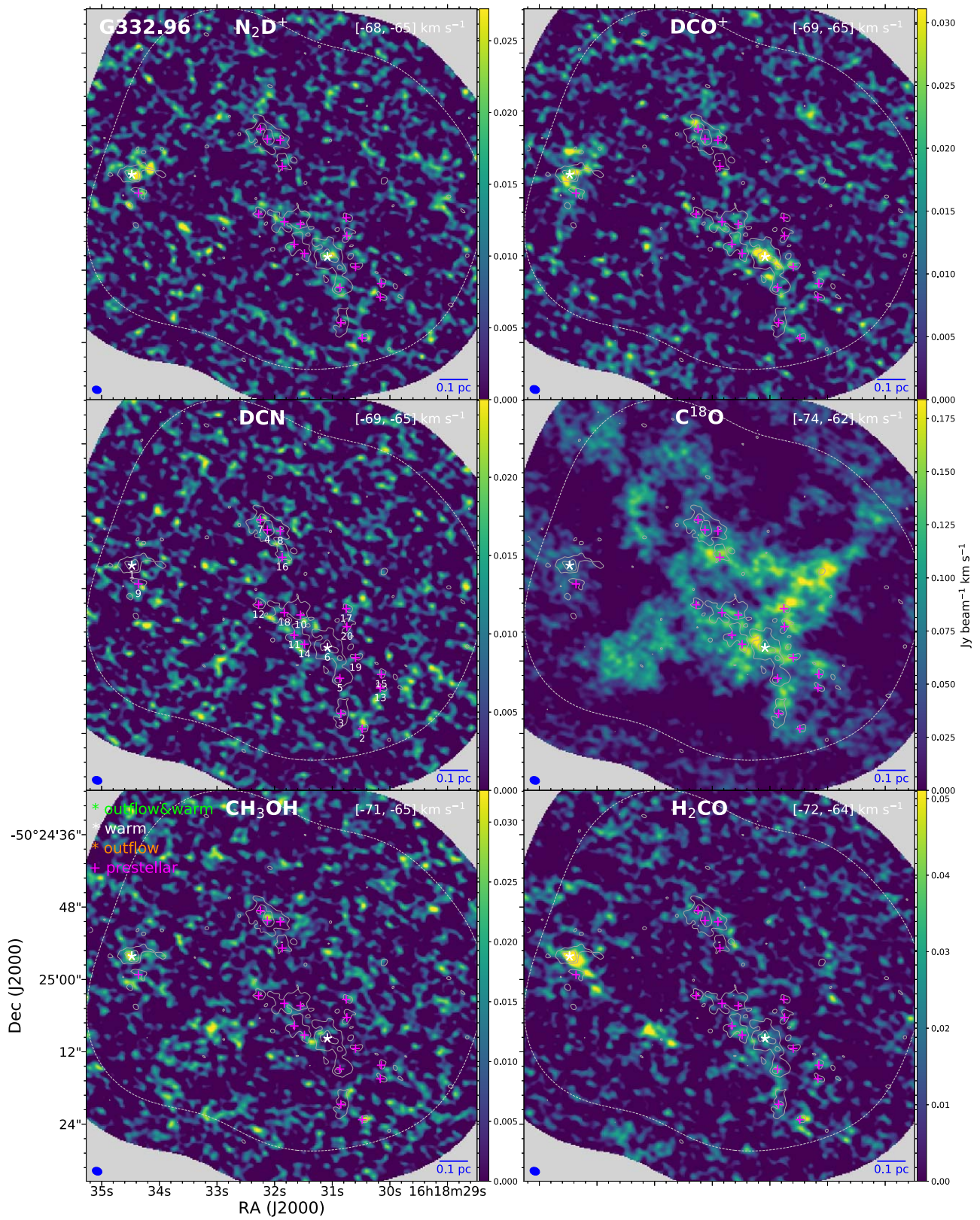


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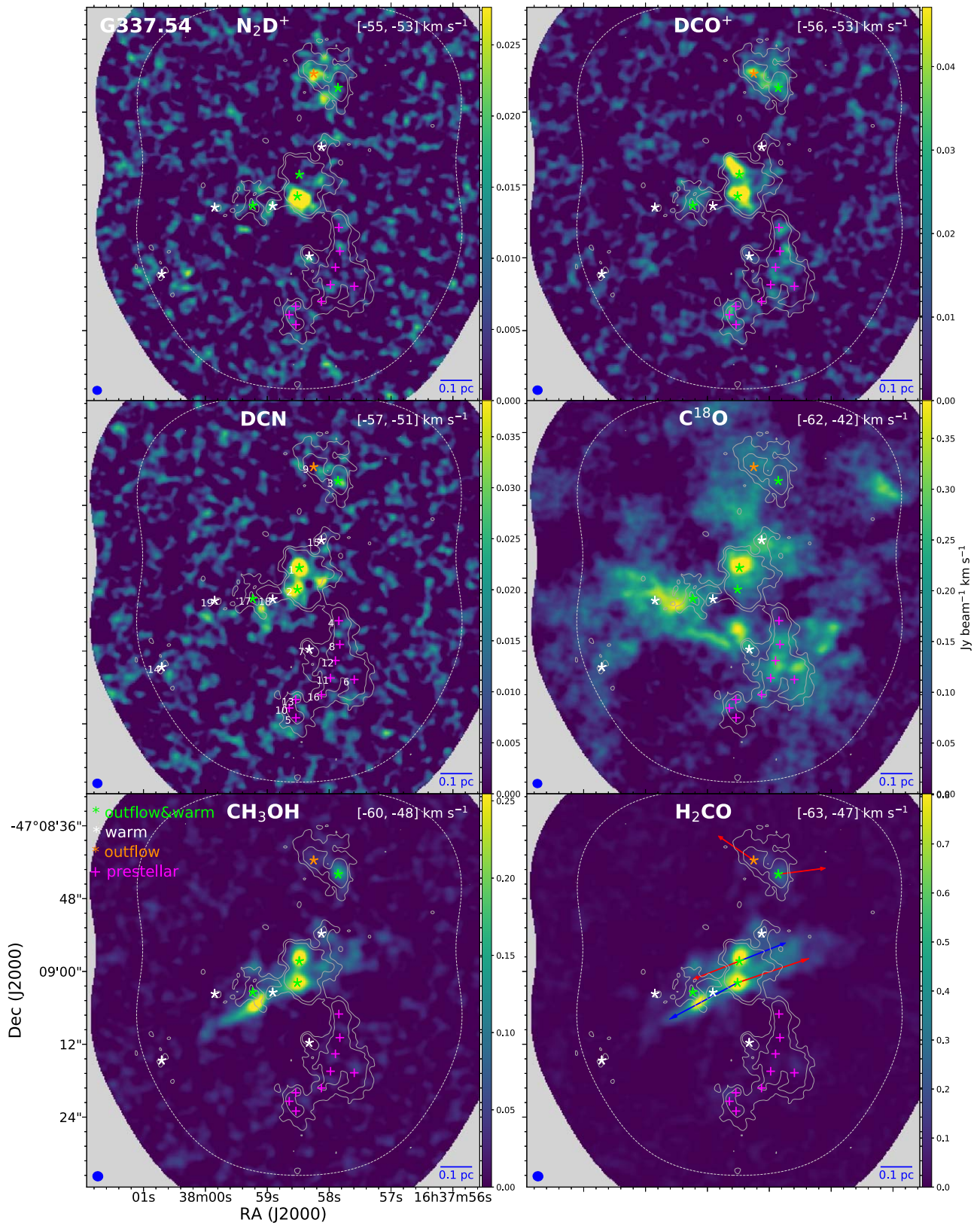


Figure 11. (Continued.)

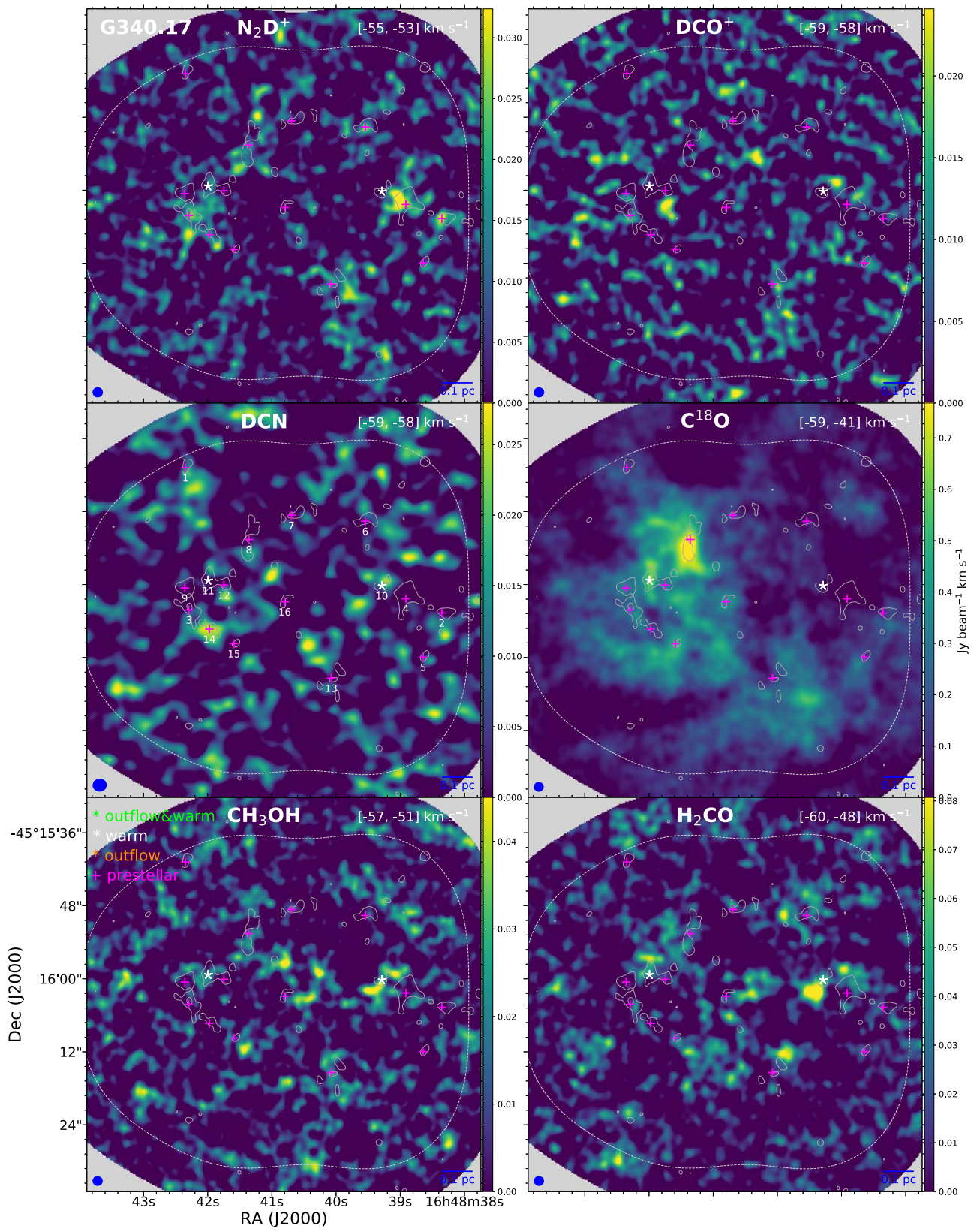


Figure 12. The same as Figure 10, but for different sources.

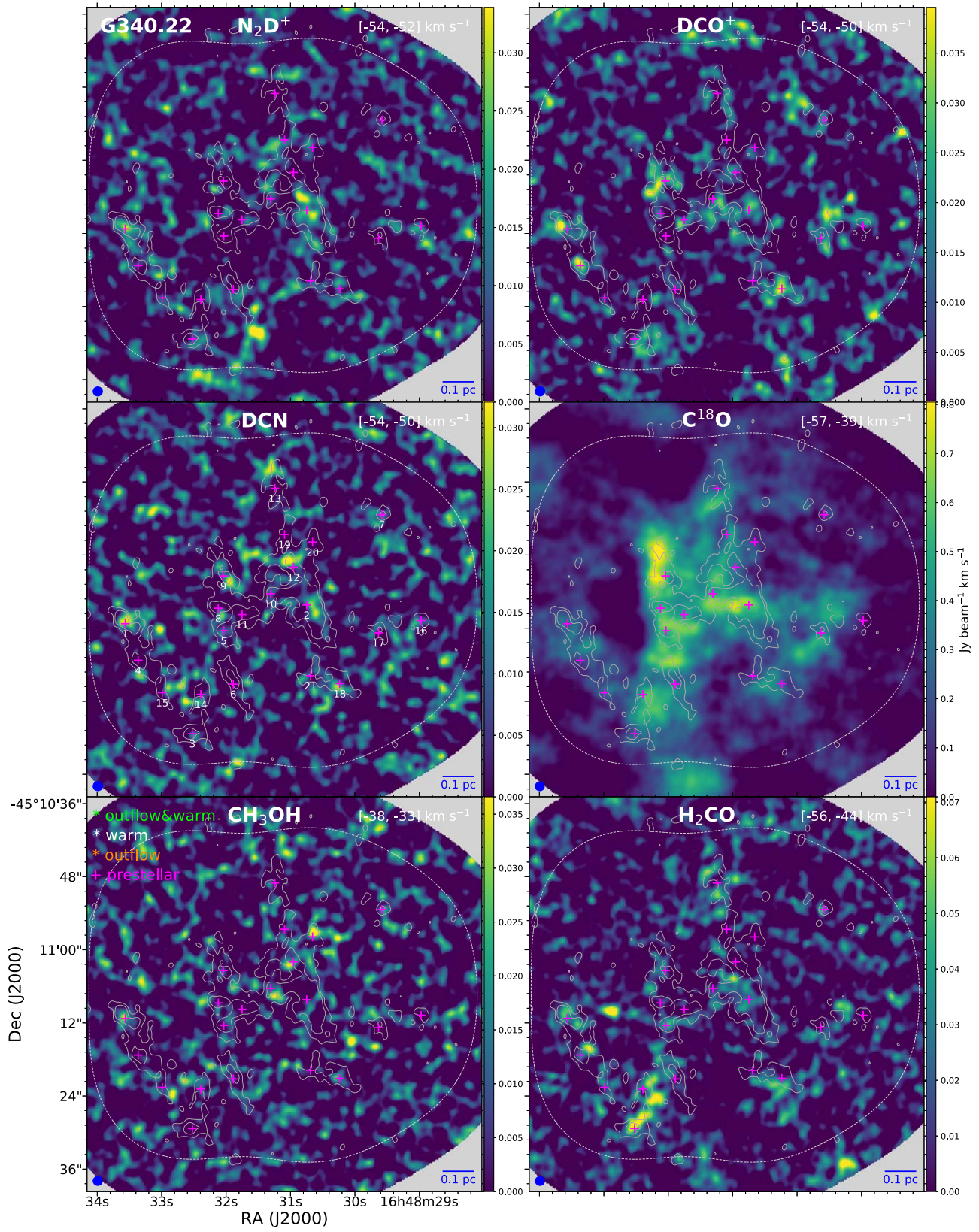


Figure 13. The same as Figure 10, but for different sources.



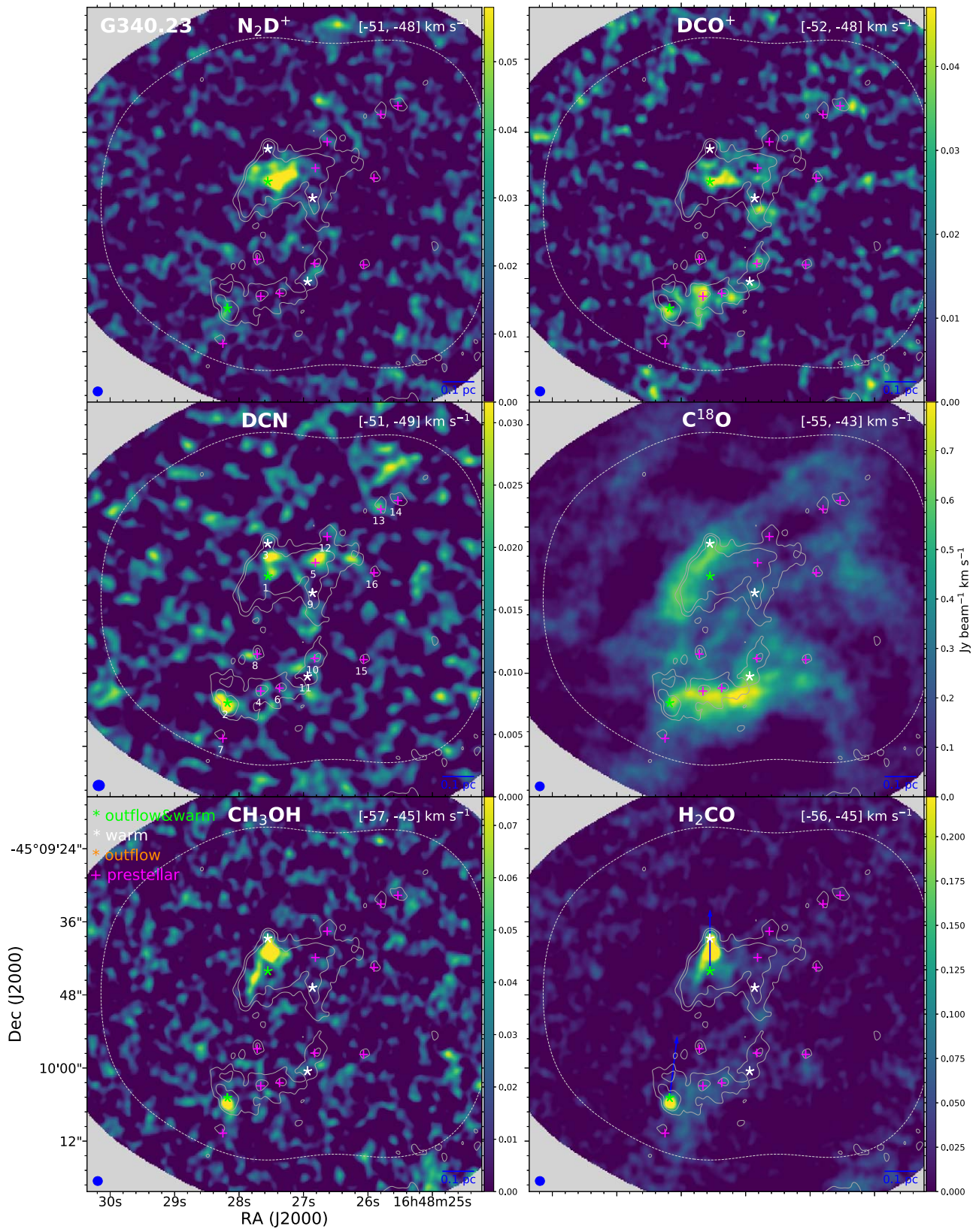


Figure 13. (Continued.)

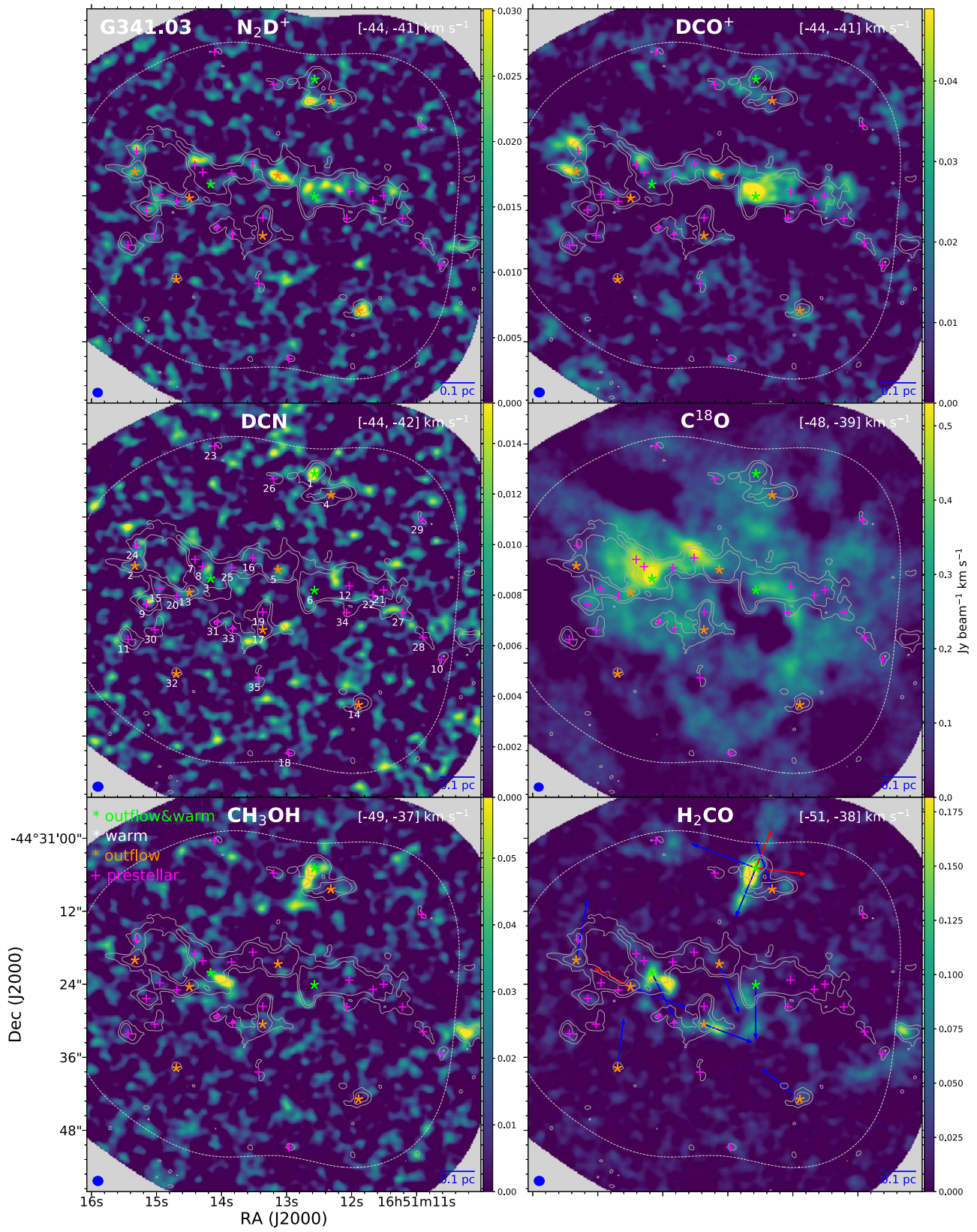


Figure 13. (Continued.)

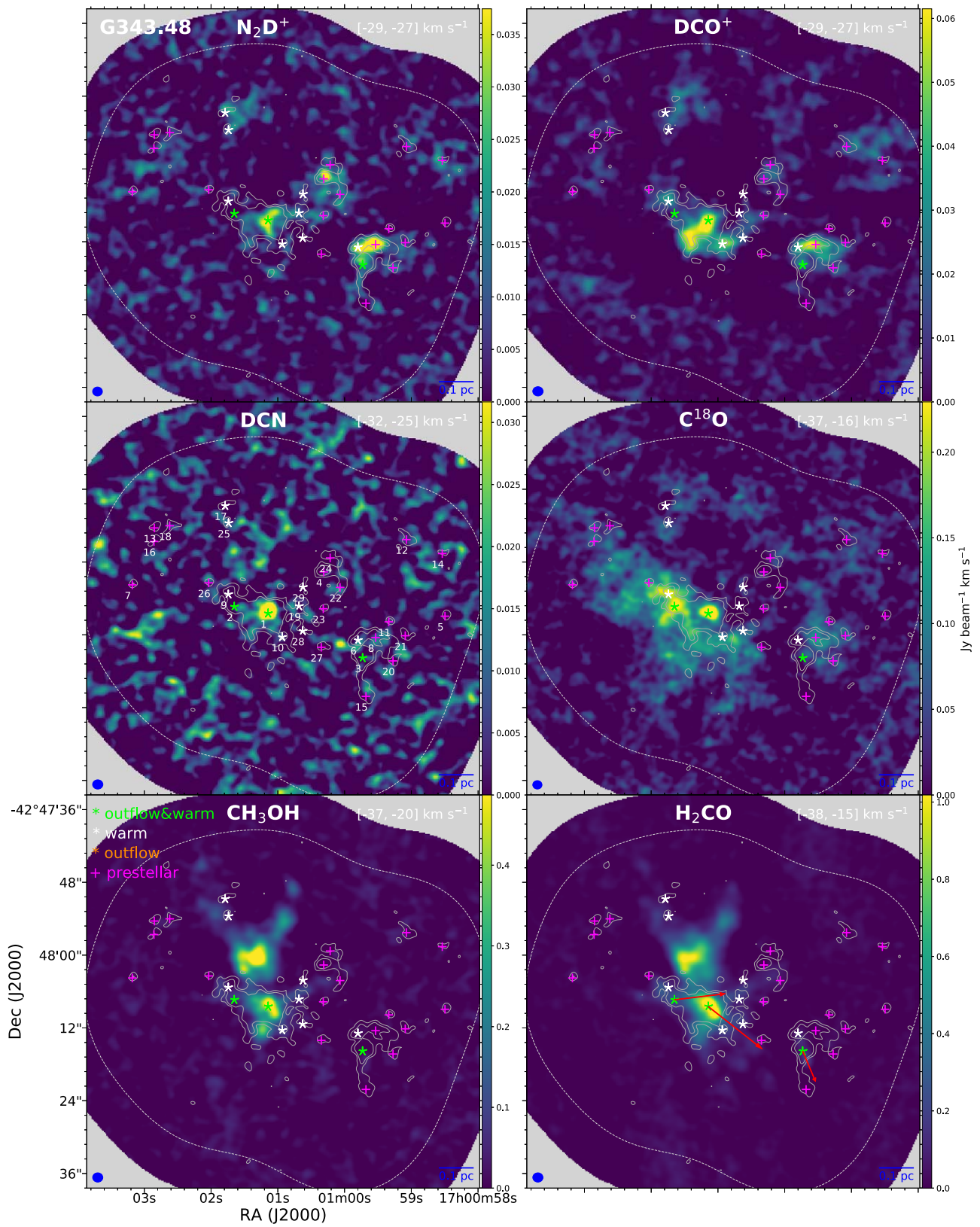
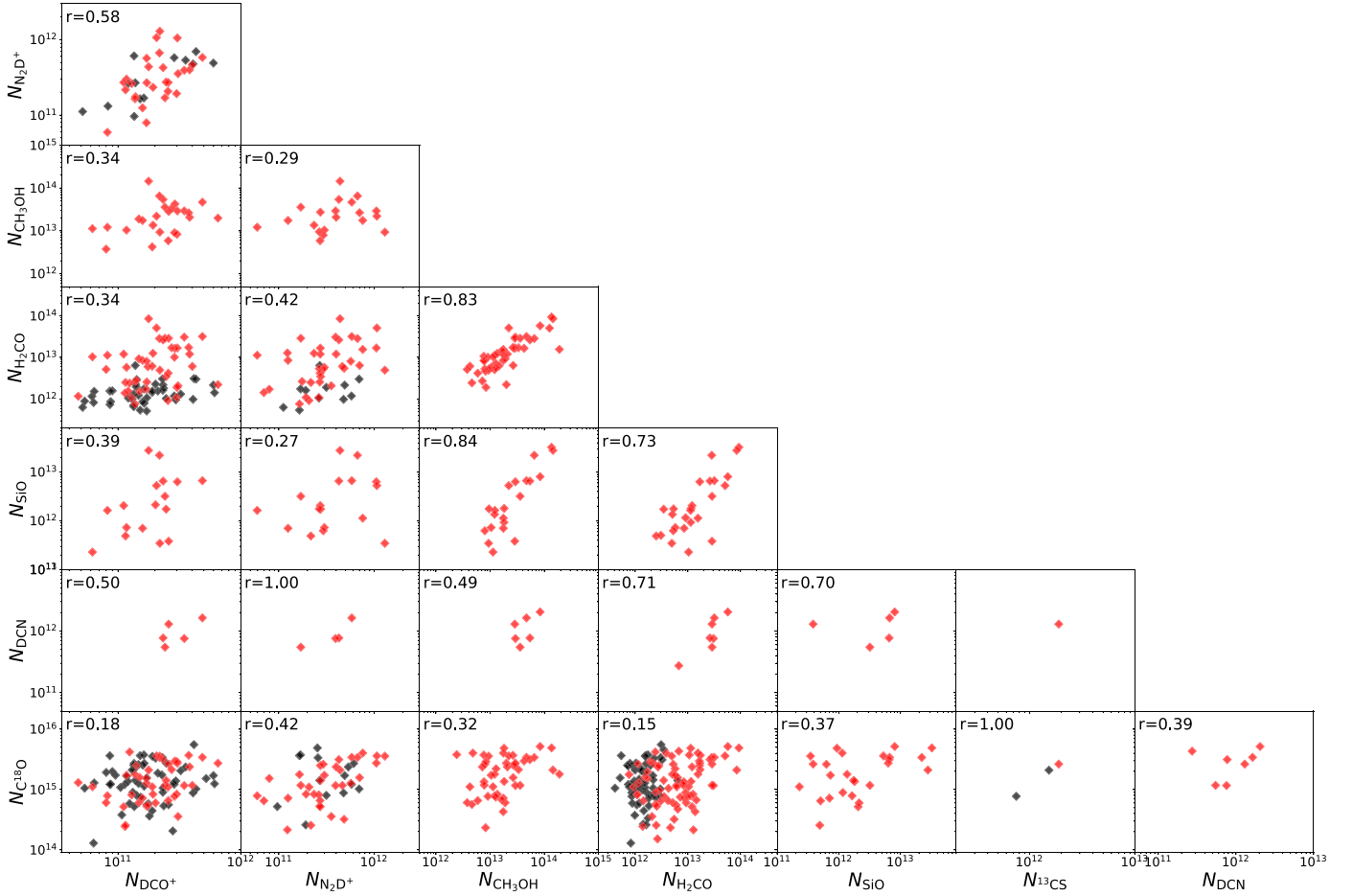


Figure 14. The same as Figure 10, but for different sources.



**Figure 15.** The column densities of each molecule plotted against each other. The black and red points represent the prestellar and protostellar cores, respectively.

**Table 5**  
Summary of the Derived Parameters of Detected Lines

Molecule	Core	$N_{\text{H}_2}$ $\times 10^{22} \text{ cm}^{-2}$	$n_{\text{H}_2}$ $\times 10^5 \text{ cm}^{-3}$	$T_{\text{NH}_3}$ K	$I_{\text{C}^{18}\text{O}}$ K	$v_{\text{C}^{18}\text{O}}$ $\text{km s}^{-1}$	$\sigma_{\text{C}^{18}\text{O}}$ $\text{km s}^{-1}$	$N_{\text{C}^{18}\text{O}}$ $\times 10^{14} \text{ cm}^{-2}$	$I_{\text{DCO}^+}$ K	$v_{\text{DCO}^+}$ $\text{km s}^{-1}$	...
G10.99	1	4.78	1.59	13.4	0.69 (0.09)	0.69 (0.09)	30.16 (0.12)	0.76 (0.12)	0.41 (0.03)	29.75 (0.03)	...
G10.99	2	8.31	7.80	12.5	0.39 (0.08)	0.39 (0.08)	29.96 (0.13)	0.49 (0.11)	...	...	...
G10.99	3	7.80	5.21	11.7	0.65 (0.04)	0.65 (0.04)	29.92 (0.07)	1.07 (0.07)	0.51 (0.05)	29.63 (0.05)	...
G10.99	4	4.41	2.80	13.0	...	...	...	...	...	...	...
G10.99	5	5.55	2.33	13.3	0.62 (0.04)	0.62 (0.04)	29.28 (0.09)	1.12 (0.09)	0.79 (0.11)	29.90 (0.03)	...
G10.99	6	5.55	5.51	13.0	...	...	...	...	...	...	...
G10.99	7	5.29	2.15	12.3	1.23 (0.05)	1.23 (0.05)	29.62 (0.04)	0.85 (0.04)	1.74 (0.07)	29.56 (0.01)	...
G10.99	8	4.92	1.59	12.2	0.80 (0.04)	0.80 (0.04)	30.13 (0.04)	0.70 (0.04)	0.44 (0.06)	29.83 (0.05)	...
G10.99	9	4.25	2.43	13.3	0.84 (0.05)	0.84 (0.05)	29.38 (0.05)	0.74 (0.05)	0.66 (0.07)	29.52 (0.04)	...
G10.99	10	3.32	1.53	11.7	...	...	...	...	0.29 (0.05)	30.46 (0.05)	...
G10.99	11	5.56	6.16	11.4	0.33 (0.06)	0.33 (0.06)	30.74 (0.23)	1.10 (0.23)	0.87 (0.16)	29.78 (0.03)	...
G10.99	12	4.85	4.61	11.3	0.53 (0.09)	0.53 (0.09)	30.14 (0.11)	0.54 (0.11)	...	...	...
G10.99	13	3.21	1.55	13.0	0.80 (0.06)	0.80 (0.06)	28.99 (0.08)	0.96 (0.08)	...	...	...
G10.99	14	3.29	2.22	13.3	0.63 (0.07)	0.63 (0.07)	29.50 (0.13)	1.03 (0.13)	0.32 (0.06)	28.76 (0.08)	...
G10.99	15	3.38	1.66	13.3	1.10 (0.09)	1.10 (0.09)	29.54 (0.08)	0.91 (0.08)	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
G343.48	23	1.06	1.35	12.9	...	...	...	...	0.38 (0.06)	-28.62 (0.02)	...
G343.48	24	1.10	0.44	13.6	...	...	...	...	0.23 (0.04)	-28.93 (0.04)	...
G343.48	25	0.84	0.47	15.2	0.18 (0.02)	-28.25 (0.15)	0.92 (0.15)	2.32 (0.51)	...	...	...
G343.48	26	0.97	1.10	13.6	1.00 (0.03)	-28.84 (0.02)	0.60 (0.02)	8.78 (0.62)	...	...	...
G343.48	27	0.73	0.58	16.3	0.46 (0.03)	-28.73 (0.04)	0.40 (0.02)	2.63 (0.25)	...	...	...
G343.48	28	0.77	0.61	16.4	0.81 (0.03)	-28.40 (0.02)	0.52 (0.02)	6.05 (0.47)	0.33 (0.05)	-28.38 (0.03)	...
G343.48	29	1.05	0.62	12.0	0.11 (0.02)	-26.20 (0.17)	0.88 (0.17)	1.52 (0.40)	...	...	...

**Note.** This table contains the column density, volume density,  $T_{\text{NH}_3}$ , and the derived parameters of the lines for each dense core.

(This table is available in its entirety in machine-readable form.)

densities. Table 5 summarizes the derived parameters of the detected lines.

## Appendix B Ammonia Excitation Temperature

The excitation temperatures were obtained using the method described in Mangum & Shirley (2015). The ammonia (1,1) and (2,2) transition spectra were modeled using five-component Gaussian models with seven parameters (systemic velocity, line width, and five amplitude parameters, one for each hyperfine component). The best-fit model parameters were obtained using scipy’s “curve\_fit” routine, using the TRF (“Trust Region Reflective”) algorithm.

From these parameters, the optical depth for the (1,1) transition,  $\tau(1, 1)$ , was calculated from the ratio of the brightness of the satellite hyperfine transitions to the main component; this was solved numerically, using scipy’s “root” routine, using the Levenberg–Marquardt algorithm to minimize the sum of squared errors of the four ratios simultaneously.

Finally, the brightness temperatures,  $T_B(1, 1)$  and  $T_B(2, 2)$ , and the optical depth were combined with the line width parameter ( $\Delta v(1, 1)$  and  $\Delta v(2, 2)$ , common to all hyperfine components) to calculate the excitation temperature,  $T_{\text{NH}_3}$ , as

$$T_{\text{NH}_3} = \frac{-41.5}{\ln \left[ \frac{-0.283 \Delta v(2,2)}{\tau(1,1) \Delta v(1,1)} \ln \left( 1 - \frac{T_B(2,2)}{T_B(1,1)} (1 - \exp[-\tau(1,1)]) \right) \right]} \quad (\text{B1})$$

The full details of this method for calculating the optical depth and excitation temperature are given in Mangum & Shirley (2015).

The error bounds for the excitation temperature were then computed using a Monte Carlo approach. For each model parameter, a randomized value was repeatedly drawn (1000 times) from a Gaussian distribution, with the mean equal to the optimal parameter value and the variance equal to the variance of the parameter estimates, as reported by the fitting routine. The optical depth and excitation temperature were then calculated using each set of randomized parameters, and the variance of the resulting distribution was calculated to yield the temperature uncertainty.

## Appendix C Column Density

Assuming LTE and thin optical depths in the molecular line, the column densities of the molecules can be calculated following Mangum & Shirley (2015):<sup>18</sup>

$$N_{\text{mol}} = \frac{3h}{8\pi^3 R S \mu^2 g_u} \frac{\exp(E_u/kT_{\text{ex}})}{\exp(h\nu/kT_{\text{ex}}) - 1} \times (J_\nu(T_{\text{ex}}) - J_\nu(T_{\text{bg}}))^{-1} \int \frac{T_B dv}{f}, \quad (\text{C1})$$

where  $h$  is the Planck constant,  $S\mu^2$  is the line strength multiplied by the square of the dipole moment,  $R$  is the relative intensity of the main hyperfine transition with respect to the rest of the hyperfine transitions,  $g_u$  is the statistical weight of the upper level,  $T_{\text{ex}}$  is the excitation temperature,  $T_{\text{bg}}$  is the background temperature,  $E_u$  is the energy of the upper state,  $\nu$

is the transition frequency,  $T_B$  is the brightness temperature,  $\int T_B dv$  is the velocity-integrated intensity,  $f$  is the filling factor, and  $Q_{\text{rot}}$  is the partition function. Here,  $f$  is assumed to be 1 and  $T_{\text{NH}_3}$  approximates the  $T_{\text{ex}}$  of the molecular lines.

The molecular column density  $N_{\text{H}_2}$ , gas mass  $M_{\text{gas}}$ , and volume density  $n_{\text{H}_2}$  are derived from the continuum emission, with

$$N_{\text{H}_2} = \eta \frac{S_\nu}{B_\nu(T) \kappa_\nu \Omega \mu m_{\text{H}}}, \quad (\text{C2})$$

$$M_{\text{gas}} = \eta \frac{F_\nu D^2}{\kappa_\nu B_\nu(T)}, \quad (\text{C3})$$

$$n_{\text{H}_2} = \frac{M_{\text{gas}}}{\frac{4}{3}\pi r^3 \mu m_{\text{H}}}, \quad (\text{C4})$$











where  $\eta = 100$  is the gas-to-dust ratio,  $S_\nu$  is the peak flux density,  $F_\nu$  is the measured integrated source flux,  $\Omega$  is the beam solid angle,  $m_{\text{H}}$  is the mass of a hydrogen atom,  $\mu = 2.8$  is the mean molecular weight of the interstellar medium (Kauffmann et al. 2008),  $\kappa_\nu$  is the dust opacity at a frequency of  $\nu$ ,  $D$  is the distance to the source, and  $r$  is the radius of the dense core. We adopted a value of  $0.9 \text{ cm}^{-2} \text{ g}^{-1}$  for  $\kappa_{1.3\text{mm}}$ , which corresponds to the opacity of thin ice mantles, and a gas density of  $10^6 \text{ cm}^{-3}$  (Ossenkopf & Henning 1994).

The flux density is converted to the brightness temperature following<sup>19</sup>

$$T_B = 1.222 \times 10^3 \frac{I}{\nu^2 \theta_{\text{maj}} \theta_{\text{min}}}, \quad (\text{C5})$$

where  $T_B$  is the brightness temperature in K,  $I$  is the flux in mJy beam<sup>-1</sup>,  $\nu$  is the frequency in GHz, and  $\theta_{\text{maj}}$  and  $\theta_{\text{min}}$  are the half-power beam widths along the major and minor axes, respectively.

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<sup>18</sup> <https://github.com/ShanghuoLi/calcul>

<sup>19</sup> <https://science.nrao.edu/facilities/vla/proposing/TBconv>

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