Spatial Variation of the Chemical Properties of Massive Star-forming Clumps

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Abstract

We selected 90 massive star-forming clumps with strong N2H+(1–0), HCO+(1–0), HCN(1–0), and HNC(1–0) emission from the Millimetre Astronomy Legacy Team 90 GHz survey. We obtained Herschel data for all 90 sources and NRAO VLA Sky Survey data for 51 of them. We convolved and regridded all images to the same resolution and pixel size and derived the temperature, H2 column density, molecules’ abundances and abundance, and ratios of each pixel. Our analysis yields three main conclusions. First, the abundances of N2H+, HCO+, HCN, and HNC increase when the column density decreases and the temperature increases, with spatial variations in their abundances dominated by changes in the H2 column density. Second, the abundance ratios between N2H+, HCO+, HCN, and HNC also display systemic variations as a function of the column density due to the chemical properties of these molecules. Third, the sources associated with the 20 cm continuum emission can be classified into four types based on the behavior of the abundances of the four molecules considered here as a function of this emission. The variations of the first three types could also be attributed to the variation of the H2 column density.

Key words: ISM: kinematics and dynamics – ISM: molecules – radio lines: ISM – stars: formation

Supporting material: figure sets

1. Introduction

Many recent studies have focused on the chemistry of massive star-forming regions at different evolutionary stages (Sakai et al. 2008, 2010, 2012; Vasyunina et al. 2011, 2012; Sanhueza et al. 2012, 2013; Hoq et al. 2013; Gerner et al. 2014; Miettinen 2014; Zhang et al. 2016). These studies did not always yield fully consistent results. Gerner et al. (2014) and Sanhueza et al. (2012) suggested that the N2H+/HCO+ abundance ratio could serve as a chemical clock for massive star formation, whereas Hoq et al. (2013) found that the N2H+/HCO+ abundance ratio shows no discernible trend from quiescent to protostellar or to H II/PDR stage. The N2H+/HCO+ abundance ratio of Gerner et al. (2014) and Sanhueza et al. (2012) even displays a different trend for the evolution.

Because these previous studies usually use the molecular data from single-point observation, their results are probably affected by the distance. On the other hand, the chemical properties of star-forming regions may be affected by the environment due to the fact that stars are formed in clusters. In two previous studies (Han et al. 2015; Zhang et al. 2016), we studied the global chemical properties of massive star-forming regions at different evolution stages, and tried our best to remove the sources affected by the environment, and then obtained much improved results. However, it is still difficult to get an accurate chemical clock for massive star-forming regions.

One possible reason may be that massive star-forming regions are very complex, because stars are usually formed in clusters. Newly formed stars have effects on the physical and chemical conditions of the nearby molecular clouds. In fact, Schilke et al. (1992) determined the HCN, HNC, and DCN abundances and estimated the kinetic temperature at 17 selected positions in the massive star-forming region OMC-1. They found that the HCN/HNC abundance ratio is very high (∼80) in the immediate vicinity of Orion-KL but declines rapidly in adjacent ridge positions down to values of ∼5. The [H13CN]/[HC15N] ratio increases from 5 to 7 to roughly 15 close to Orion-IRc2. Tafalla et al. (2006) obtained the radial profile of abundances for 13 molecules in small star-forming regions for L1498 and L1517B. They found most abundance profiles can be described with simple step functions with a constant value in the outer layers and a central hole. However, there are too few such observational studies to give a statistically reliable result.

As the chemistry of star-forming regions is very sensitive to prevailing physical conditions (the temperature, density, and ionization degree), understanding the chemical composition is of great importance in order to reveal the physics of the early stages of massive star formation. Spatial variations of the chemistry reflect the response of the molecular emission to different physical and chemical environments that characterize the star-forming clumps.

In this work, we select 90 massive star-forming clumps with relatively strong molecular line emission (see Tables 1 and 2) from Zhang et al. (2016) and study the spatial variations of the chemical properties of massive star-forming regions. We propose that a good chemical clock cannot be achieved from either the data of single-point observation or the data averaged from the whole source. We describe our archive data in Section 2 and data reduction and results in Section 3. We discuss the spatial variations of the abundances and abundance ratios with the temperature and column density, the effect of 20 cm continuum emission on the abundances, and abundance ratios in Section 4. We summarize our findings in Section 5.

2. Archive Data

2.1. The ATLASGAL Survey

The Atacama Pathfinder Experiment (APEX) Telescope Large Area Survey of the Galaxy (ATLASGAL) survey was
The first systematic survey of the inner Galactic plane in the submm band that traces the thermal emission from dense clumps at 870 μm and is complete for all massive clumps above 1000M☉ to the far side of the inner Galaxy (~20 kpc). The survey was carried out with the Large APEX Bolometer Camera (Schuller et al. 2009), which is an array of 295 bolometers observing at 870 μm (345 GHz). At this wavelength, the APEX Telescope has a FWHM beam size of 19″.2. The survey region covered the Galactic longitude region of |l| < 60° and 280° < l < 300° and the Galactic latitude region of |b| < 1°5 and −2° < l < 1°, respectively. Urquhart et al. (2014) presented a compact source catalog of this survey, which consists of ~10,163 sources and is 99% complete at a ~6σ flux level, which corresponds to a flux sensitivity of ~0.3–0.4 Jy beam$^{-1}$.

2.2. The MALT90 Survey

The Millimetre Astronomy Legacy Team 90 GHz (MALT90) survey is a large international project that exploited...
the fast-mapping capability of the Australia Telescope National Facility Mopra 22 m telescope and obtained 16 molecular line maps near 90 GHz in order to characterize the physical and chemical conditions of high-mass star formation regions over a wide range of evolutionary states (from prestellar cores to protostellar cores and to H II regions). The sample of this survey is a subsample of the ATLASGAL catalog. The angular and spectral resolution of this survey are about 36′ and 0.11 km s\(^{-1}\) (Jackson et al. 2013). The MALT90 data has been obtained from the online archive.6

### 2.3. The NVSS Survey

The NRAO VLA Sky Survey (NVSS) is a continuum survey, which covers the entire sky north of 40° decl. at 1.4 GHz. The angular resolution is about 45′, and the noise level in the images is about 0.5 mJy/beam. A detailed description of the survey can be found in Condon et al. (1998). In this paper, we use images provided by the home page of NVSS.7

### 2.4. The GLIMPSE and MIPS Survey

The Galactic Legacy Infrared Mid-Plane Survey Extraordinaire (GLIMPSE) survey is a mid-infrared survey (3.6, 4.5, 5.8, and 8.0 μm) of the Inner Galaxy performed with the Spitzer Space Telescope (Benjamin et al. 2003). The angular resolution is better than 2″ at all wavelengths. GLIMPSE covers 5° ≤ |l| ≤ 65° with |b| ≤ 1°, 2 ≤ |l| < 5° with |b| ≤ 1.5°, and |l| < 2° with |b| ≤ 2°. The MIPS/Spitzer Survey of the Galactic Plane (MIPSGL) is a survey of the same region as GLIMPSE at 24 and 70 μm, using the Multiband Imaging Photometer (MIPS) aboard the Spitzer Space Telescope (Rieke et al. 2004). The angular resolution at 24 and 70 μm is 6′ and 18′, respectively.

### 2.5. The Hi-GAL Survey

The Herschel Infrared Galactic (Hi-GAL) Plane Survey is an Open Time Key Project on board the Herschel Space Observatory (Pilbratt et al. 2010), which mapped the inner Galaxy at 70 and 160 μm with Photoconductor Array Camera and Spectrometer (PACS; Poglitsch et al. 2010) and at 250, 350, and 500 μm with the Spectral and Photometric Imaging Receiver (SPIRE; Griffin et al. 2010). The spatial resolution of the images are 6″, 12″, 18″, 24″, and 35″ for the five wavelength bands (Molinari et al. 2010), respectively.

## Table 3

| Survey        | Frequency (Wavelength) | Facility       | Purpose Here                  | Citation                  |
|---------------|------------------------|----------------|-------------------------------|----------------------------|
| ATLASGAL      | 345 GHz                | APEX           | H₂ column density             | Schuller et al. (2009)     |
| MALT90        | 90 GHz                 | Mopra          | Molecules’ abundances         | Jackson et al. (2013)      |
| NVSS          | 1.4 GHz                | VLA            | Tracer of UV radiation        | Condon et al. (1998)       |
| GLIMPSE       | 3.6, 4.5, 5.8, and 8.0 μm | Spitzer       | Tracer of star formation      | Benjamin et al. (2003)     |
| MIPS          | 24 and 70 μm           | Spitzer        | Tracer of star formation      | Rieke et al. (2004)        |
| Hi-GAL        | 70, 160, 250, 350, and 500 μm | Herschel   | Dust temperature              | Molinari et al. (2010)     |

### Note

We list the project name in column 1, the frequency or wavelength in column 2, the facility in column 3, the purpose for using the corresponding data in column 4, and the citation in column 5.

Finally, we summary the character properties of above five surveys and what purposes we use these data in this work in Table 3.

## 3. Results

### 3.1. The Distribution of the Dust Temperature and Column Density

Assuming the dust emission is optically thin for the Herschel data at 160, 250, 350, and 500 μm, we use these data to derive the distributions of the temperature and column density of 90 massive star-forming clumps. To obtain the distribution of the dust temperature, we convolved and regridded the 160, 250, and 350 μm images to the lowest resolution of 35″ and largest pixel size of 11″/5 of the 500 μm image and then performed spectral energy distribution (SED) fitting pixel-by-pixel. We used a gray body function for a single temperature as following (Ward-Thompson & Robson 1990) to estimate the temperature of each pixel:

\[
F_\nu = \frac{\Omega B\nu(T_{\nu})}{B\nu(T_{\nu})} \left(1 - e^{-\tau}\right),
\]

where \(\Omega\) is the effective solid angle corresponding to each pixel and \(B\nu(T_{\nu})\) is the Planck function at dust temperature \(T_{\nu}\), which is defined as \(B\nu(T_{\nu}) = \frac{2h\nu^3}{c^2}\exp(\frac{h\nu}{kT_{\nu}}) - 1\)^\(-1\), where \(h\) is the Planck constant, \(\nu\) is the frequency, \(c\) is the speed of light, and \(k\) is the Boltzmann constant. The optical depth, \(\tau\), is given by the relation \(\tau = (\nu/\nu_c)^{\beta}\), where \(\beta = 2\) is the dust emissivity index, and \(\nu_c\) is the critical frequency at which \(\tau = 1\). We assigned an uncertainty of 20% to each Herschel flux and used it as a calibration error (Faimali et al. 2012).

We display the distributions of temperatures for 90 sources in Figure 1 online.

Subsequently, the ATLASGAL 870 μm images were also convolved and regridded to the resolution and pixel size of the 500 μm image. The hydrogen molecular column density distribution of each source was then calculated pixel-by-pixel:

\[
N_{H_2} = \frac{S_\nu R}{B_\nu(T_{\nu})\Omega k_{\nu_1}\mu m_{1H}},
\]

where \(S_\nu\) is the total 870 μm flux density over the line-emitting area; \(R\) is the gas-to-dust mass ratio, which is assumed to be 100; \(\Omega\) is the solid angle; \(\mu\) is the mean molecular weight of the interstellar medium, which is assumed to be 2.8; \(m_{1H}\) is the mass of a hydrogen atom; \(B_\nu\) is the Planck function for dust temperature \(T_{\nu}\); and \(k_{\nu_1}\) is the dust-absorption coefficient, taken as 1.85 cm\(^2\) g\(^{-1}\) (interpolated to 870 μm from column 5 of Table 1 of Ossenkopf & Henning 1994).
We thus obtained the distributions of the H$_2$ column density for 90 sources and show them in Figure 1 online.

With an examination of temperature and H$_2$ column density distributions (Figure 1 online) and the corresponding three-color images (in Figure 2 online, we show the three-color images from Spitzer data at 3.6, 8 and 24 $\mu$m for all 90 sources), we found that the temperature is usually higher at the center of the clump where the H$_2$ column density is high for the sources in which there is star formation. Conversely, the temperature is lower at the center of the clump where no stars are being formed. Figure 1 shows temperature and column density distributions of source 82 as an example. It is clear that the temperature is lower when the column density is higher. This indicates that the more diffuse outer regions of the clump may be heated by interstellar ultraviolet (UV) radiation and cosmic rays. It is hot where the extinction is small. The very high temperature regions in the top left corner of Figure 1 suggest the presence of an infrared bubble.

3.2. The Distribution of Abundances and Abundance Ratios

Following Sanhueza et al. (2012), we derived the optical depth of each pixel using the formula

$$ T_{mb} = f (T_{ex} - T_{bg}) (1 - e^{-\tau_\nu}) , $$

where $T_{mb}$ is the main beam brightness temperature, $f$ is the filling factor, $\tau_\nu$ is the optical depth of the line, $T_{bg}$ is the background temperature, and $J(T) = \frac{h e}{k (e^{hT/k} - 1)}$, where $h$ is the Planck constant, and $k$ is the Boltzmann constant. To determine the optical depth of the line, the excitation temperature ($T_{ex}$) of the line was assumed to be equal to the dust temperature ($T_D$).

Then, the column density of each pixel was calculated based on the averaged molecular spectra of N$_2$H$^+$, HCO$^+$, HCN, and HNC of each pixel by assuming local thermodynamic equilibrium, using the following formula from Garden et al. (1991):

$$ N = \frac{3 k}{8 \pi B_{J} \mu^2 R} \frac{(T_{ex} + hB/3k)}{(J + 1)} \frac{\exp(E_J/kT_{ex})}{[1 - \exp(-h\nu/kT_{ex})]} \int \tau_\nu dv , $$

where $\nu$ is the transition frequency and is assumed as 1, $\tau_\nu$ is the optical depth of the line, $\mu$ is the permanent dipole moment of the molecule, and $R$ is the relative intensity of the brightest hyperfine transition with respect to the others. $R$ is only relevant for hyperfine transitions because it considers the satellite lines corrected by their relative opacities. $R = 5/9$ for N$_2$H$^+$, 1 for HCO$^+$ and HNC, and 3/5 for HCN. $J$ is the rotational quantum number of the lower state, $E_J = hBJ(J + 1)$.
is the energy in level $J$, and $B$ is the rotational constant of the linear molecule in question. The dipole moment and rotational constant of these four molecules are shown in Table 3 of Zhang et al. (2016).

We thus derived the column densities of $N_2H^+$, HCO$^+$, HCN, HNC, and their abundance distributions for all 90 sources. We display the abundance distributions for all 90 sources in Figure 3 online. We also calculated the abundance ratios between these four molecules for each source and display their distributions in Figure 4 online.

The results in Figures 3 and 4 online indicate that spatial variations of the abundance and abundance ratio in massive star-forming clumps are complex, making it difficult to describe them clearly in a unified way. Figure 3 includes sources 82 and 15; they have been separated by their names. Each source has several small panels named as (a), (b), (c), and (d) and shows the abundance distributions of $N_2H^+$, HCO$^+$, HCN, and HNC for sources 82 and 15, respectively. By comparing the distributions of abundance in Figure 3 and the distributions of the temperature and column density in Figure 1, we clearly see that the abundances of these four molecules are usually higher at edges of the clump where the density is lower and the temperature is higher, and they are usually lower at the center of the clump where the conditions are opposite. However, the spatial variations of the abundance ratios of these molecules seem to be complex (see Figure 4). The abundance ratio of HCN/HNC is large in eastern edge of the clump, and it seems to decrease from the eastern edge to the western edge of the clump. By contrast, the abundance ratio of HCO$^+$/HNC is small in the eastern edge of the clump and increases from the eastern edge to the western edge of the clump. The abundance ratio of HCO$^+$/HCN is large in the eastern, northern, and western edges of the clump and is small in the center and southern part of the clump. These results suggest both HCN and HCO$^+$ abundances increase toward the eastern edge of the clump, with HCN increasing more rapidly than HCO$^+$. Conversely, the HNC abundance may decrease in the eastern edge. The abundance ratios of $N_2H^+$/HCN, $N_2H^+$/HCO$^+$, and $N_2H^+$/HNC display similar spatial variations, with ratios being large in the center and western part of the clump. The results support the idea that HCN and HCO$^+$ abundances increase rapidly in the eastern edge and may also indicate that the $N_2H^+$ abundance decreases in the eastern edge more rapidly than the HNC abundance does.

4. Discussion
4.1. The Chemical Properties of $N_2H^+$, HCO$^+$, HCN, and HNC
4.1.1. HCN and HNC
Past observations show that HCN is a widely used dense gas tracer, and HNC is a reliable tracer of cold gas (Schilke et al. 1992). The abundances of CN, HCN, and HNC are sensitive to temperature, optical depth, and UV radiation (Schilke et al. 1992; Fuente et al. 1993; Boger & Sterngren 2005). HNC transfers to HCN at high temperatures. Therefore, the abundance ratio of HCN/HNC is strongly dependent on the temperature (Ungerechts et al. 1997; Vasyunina et al. 2011). The abundance ratio of HCN/HNC is $\sim$1 for infrared dark clouds (IRDCs; Vasyunina et al. 2011), is higher and reaches up to $\sim$13 for high-mass protostars (HMPOs; Helmich & van Dishoeck 1997), and is $\sim$80 for very warm regions like Orion (Goldsmith et al. 1986; Schilke et al. 1992). Gas-phase chemical models suggest that HCN and HNC are primarily produced via the dissociative recombination reaction (Herbst 1978):

$$\text{HCNH}^+ + e^- \rightarrow \text{HCN} + H \text{ or } \text{HNC} + H.$$  

The resulting HNC/HCN abundance ratio is predicted to be 0.9 in this case. HNC has a unique formation via the reactions (Pearson & Schaefer 1974; Allen et al. 1980):

$$\text{H}_2\text{CN}^+ / \text{H}_2\text{NC}^+ + e^- \rightarrow \text{HNC} + H.$$  

As a result of this additional HNC production channel, the HNC/HCN ratio can rise above unity (Miettinen 2014).

4.1.2. $N_2H^+$
Owing to its resistance to depletion at low temperatures and high densities, $N_2H^+$ is an excellent tracer of cold and dense molecular clouds. It is primarily formed through the gas-phase reaction

$$\text{H}_3^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}_2.$$  

When there are CO molecules in the gas phase, they can destroy $N_2H^+$ and produce HCO$^+$ through reaction (Miettinen 2014)

$$N_2\text{H}^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{N}_2.$$  

4.1.3. HCO$^+$
HCO$^+$ is a highly abundant molecule, with its abundance especially enhanced around regions of higher fractional ionization. It can also be enhanced by the presence of outflows where shock-generated radiation fields are present (Vasyunina et al. 2011). In dense molecular clouds, HCO$^+$ is mainly formed through the gas-phase ion-neutral reaction (Herbst & Klemperer 1973)

$$\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2.$$  

When the shock heats the gas and produces UV radiation through Ly$\alpha$ emission ($\lambda = 121.6$ nm), the icy grain mantles evaporate and the HCO$^+$ abundance is enhanced because of evaporated CO and H$_2$O, which can form HCO$^+$ in the reaction with photoionized carbon (Rawlings et al. 2000, 2004):

$$\text{C}^+ + \text{H}_2\text{O} \rightarrow \text{HCO}^+ + \text{H}.$$  

4.2. The Spatial Variations of the Abundances
We studied the abundance variations of $N_2H^+$, HCO$^+$, HCN, and HNC as a function of the column density and temperature pixel-by-pixel. Figure 5 online shows the results of all 90 sources. In general, the temperature ranges from 16 to 26 K, and the column density ranges from $10^{22}$ to $10^{24}$ cm$^{-2}$. The abundances of $N_2H^+$, HCO$^+$, HCN, and HNC range from $10^{-10}$ to $10^{-8}$, depending on the source. Abundances of $N_2H^+$, HCO$^+$, HCN, and HNC often show an obvious increasing trend with a decreasing column density and a relatively weak but also obvious increasing trend with an increasing temperature.

By checking the three-color images of 90 sources (Figure 2 online), we found out that some sources overlap with the bubbles along the line of sight. These bubbles are usually large with sizes similar to that of clumps and show strong 8 and...
Figure 3. The abundance distributions of N$_2$H$^+$, HCO$^+$, HCN, and HNC of source 82 (G354.945-0.539, an example of Group I) and source 15 (G12.774+0.337, an example of Group II, was classified into the fourth type) in gray scale. The black bars show the units of abundance in log.
(The complete figure set (90 images) is available.)
24 μm emission. The abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC of these sources usually display an obvious increasing trend as a function of the decreasing H$_2$ column density, but with relatively larger dispersion. We classified these sources into Group II (see Tables 1 and 2). Other sources, however, are relatively isolated star-forming regions. Some contain small H II or infrared bubbles excited by their own star formation. The abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC clearly rise when the H$_2$ column density decreases and with smaller dispersion. We classified these sources into Group I (see Tables 1 and 2). We summarize the abundance variation of Group I and II sources with the H$_2$ column density and temperature in Table 4.

We display source 82 as an example of Group I in Figure 5. The abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC are clearly seen to display an obvious increasing trend with the decreasing column density and increasing temperature. We find that (1) while the H$_2$ column density is inversely proportional to the temperature, the pixels with higher column densities tend to have lower temperatures; (2) abundances of these four molecules reach the minimum in the pixels with lowest temperatures and largest column densities; and (3) the abundance of N$_2$H$^+$ displays a weak increasing trend with the decreasing column density and increasing temperature.

Table 4. We Classified 90 Sources into Group I and II (See Details in Section 4.2)

| Type   | Environment | Abundance with N(H$_2$) | Abundance with T |
|--------|-------------|-------------------------|-----------------|
| Group I| Isolated    | Decreasing (obvious)    | Increasing (weak) |
| Group II| Near bubbles| Decreasing (obvious)    | Increasing (weak) |

Note. Here we display the variation trend of the molecules’ abundances with the H$_2$ column density and temperature for Group I and II sources, respectively.

The distributions of the abundance ratio between N$_2$H$^+$, HCO$^+$, HCN, and HNC for source 82 (G354.945−00.539) in gray scale. The black bars show the units of the abundance ratio in log. (The complete figure set (90 images) is available.)

Figure 4. The distributions of the abundance ratio between N$_2$H$^+$, HCO$^+$, HCN, and HNC for source 82 (G354.945−00.539) in gray scale. The black bars show the units of the abundance ratio in log. (The complete figure set (90 images) is available.)
Figure 5. The abundances of $\text{N}_2\text{H}^+$, $\text{HCO}^+$, HCN, and HNC as a function of the H$_2$ column density and temperature for source 82 (G354.945-00.539, an example of Group I) and source 15 (G12.774+00.337, an example of Group II) was classified into the fourth type, respectively. (The complete figure set (90 images) is available.)
tend to have lower column densities, we conclude that the result also could be attributed the fact that the abundances of these molecules are mainly dominated by the H$_2$ column density. We show source 15 as an example of Group II sources in Figure 5. The abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC increase as the H$_2$ column density decreases. This suggests that their abundance variations were also dominated by the H$_2$ column density. However, the dispersion of abundances corresponding to the same H$_2$ column density becomes larger. Such dispersion also increases as the H$_2$ column density decreases. This is probably due to the effect of active star formation near it, because the chemistry is sensitive to the temperature, density, and ionization degree. Group II sources are associated with an infrared bubble, which is excited by a group of OB stars. These OB stars affect the temperature and ionization degree by strong UV radiation, shock, and heat. Such an effect is more remarkable in the low column density regions where the extinction is small. As shown from Figure 5, for the pixels with the same column density, those with higher abundances tend to have higher temperatures. Figure 3 shows that the abundance distributions of N$_2$H$^+$, HCO$^+$, HCN, and HNC of source 15 are similar to those of source 82. The abundances are low in the center and high in the edge of the clump. However, the abundance distributions of these four molecules show obvious asymmetry in source 15. All of them reach the maximum values in the southern edge of the clump. This indicates that the clump chemistry was affected by the environment in this direction. The abundance of HCN in the whole map increases greatly compared with that of source 82. This is consistent with the fact that source 15 has a higher temperature.

4.3. The Spatial Variation of the Abundance Ratios

The abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC are affected by the H$_2$ column density and environment to a great extent. It is more helpful to study the spatial variations of the abundance ratios between these molecules. We show source 82 as an example of Group I sources (see Figure 6). The abundance ratio of HCN/HNC shows a similar increasing trend as a function of the decreasing H$_2$ column density and increasing temperature. This is consistent with previous result that HNC transfers into HCN at higher temperatures, and the abundance ratio of HCN/HNC is strongly dependent on the temperature (Vasyunina et al. 2011). The abundance ratios of HNC/HCN, HNC/HCO$^+$, HCO$^+$/HCN, N$_2$H$^+$/HCO$^+$, N$_2$H$^+$/HCN, and N$_2$H$^+$/HNC increase as the H$_2$ column density increases and the temperature decreases. Such results suggest that increasing the H$_2$ column density and decreasing the temperature result in an observed decrease in the abundances (in order of rapidity from highest to lowest) HCN, HCO$^+$, HNC, and N$_2$H$^+$ (see Table 5).

We show source 15 as an example of Group II sources. The abundance ratios of HNC/HCN, HNC/HCO$^+$, HCO$^+$/HCN, N$_2$H$^+$/HCO$^+$, N$_2$H$^+$/HCN, and N$_2$H$^+$/HNC show only a weak increasing trend as a function of the increasing H$_2$ column density and decreasing temperature (see Figure 6). This is consistent with the fact that their abundances have larger dispersions due to the environmental effect.

For sources 82 and 15, those abundance ratios show obvious increasing trends with the increasing H$_2$ column density and decreasing temperature. However, this is not true for all Group I and II sources. Although a number of Group I and II sources display similar trends for abundance ratios as sources 82 and 15 do, many of them do not show a clear correlation between the abundance ratios and the H$_2$ column density and temperature (see Figure 6 online). This may be attributed to the complex environment of massive star-forming regions.

4.4. The Correlation between the Column Density of H$_2$ and those of N$_2$H$^+$, HCO$^+$, HCN, and HNC

Figure 7 online displays the correlations between the H$_2$ and N$_2$H$^+$, HCO$^+$, HCN, and HNC column densities pixel-by-pixel for 90 sources. For most sources of our sample (e.g., source 55 in Figure 7), the correlations between the H$_2$ column density and N$_2$H$^+$, HCO$^+$, HCN, and HNC column densities are relatively complex. When the H$_2$ column density is lower than a threshold value, the H$_2$ column density displays an inversely linear correlation with N$_2$H$^+$, HCO$^+$, HCN, and HNC column densities, respectively. On the other hand, when the H$_2$ column density is higher than the threshold value, the N$_2$H$^+$, HCO$^+$, HCN, and HNC column densities tend to be higher. These sources usually overlap with the infrared bubble or contain a small infrared bubble (see Figure 2 online). This indicates that the infrared bubble inside the clump or nearby may affect the abundance of these molecules.

For other sources of our sample (e.g., source 51 in Figure 7 online), the H$_2$ column density displays an obvious decreasing trend as molecules’ column densities increase. The correlation is nearly linear. This clearly shows that column densities of N$_2$H$^+$, HCO$^+$, HCN, and HNC detected at pixels with high H$_2$ column densities are larger than those detected at pixels with high H$_2$ column densities. Three-color images of these sources (see Figure 2 online) suggest that there is no infrared bubble inside or nearby.

Figure 7 online clearly shows that, whether there is feedback from star formation or not, the column density variations of N$_2$H$^+$, HCO$^+$, HCN, and HNC are much smaller than that of H$_2$ column densities. Their abundances are dominated by H$_2$ column densities.

4.5. The Effect of 20 cm Continuum Emission on Abundances and Abundance Ratios

Since 20 cm continuum emission usually indicates the appearance of OB stars, their feedback may affect the chemistry of nearby molecular clumps. We used 20 cm continuum emission data of 70 sources from the NVSS survey and convolved and regridded them into the resolution and pixel size of 500 $\mu$m data of the Herschel survey. Finally, 51 sources have more than 10 pixels overlapping with the 20 cm continuum emission (see Table 1). We display the distribution of the 20 cm continuum emission of these 51 sources in Figure 9 online, plot the 20 cm continuum emission flux as a function of abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC for 51 sources in Figure 8 online, and plot the 20 cm continuum emission flux as a function of abundance ratios, respectively, in Figure 10 online. From an examination of Figure 8 online, we found that they could be classified into four types (see Table 1). We simply called them the first, second, third, and fourth type and discuss their properties, respectively, below.

4.5.1. The First Type

For the first type, the abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC decrease as a function of an increasing 20 cm
continuum emission flux (see Table 6). We show source 40 as an example in Figure 8. When we check the abundance distributions of $\text{N}_2\text{H}^+$, HCO$^+$, HCN, and HNC of source 40 in Figure 3 online and the distribution of 20 cm continuum emission in Figure 9, it is evident that the abundances of HCO$^+$, HCN, and HNC are larger when they are far away from the 20 cm continuum emission peak. The distribution of the $\text{N}_2\text{H}^+$ abundance is much different from that of the other three molecules. It mainly appears in the northern part of the mapping region. The reason is still unclear.

Figure 6. The abundance ratios HCN/HNC, HCO$^+$/HCN, HCO$^+$/HNC, N$_2$H$^+$/HCN, N$_2$H$^+$/HCO$^+$, and N$_2$H$^+$/HNC as a function of the H$_2$ column density and temperature for source 82 (G354.945-00.539, an example of Group I) and source 15 (G12.774+00.337, an example of Group II, was classified into the fourth type). (The complete figure set (90 images) is available.)
We display the abundance ratios between N$_2$H$^+$, HCO$^+$, HCN, and HNC as a function of the 20 cm continuum emission flux for source 34 in Figure 10. Only the abundance ratio of N$_2$H$^+$/HNC shows a weak trend of rising as the 20 cm continuum emission flux decreases. This indicates that N$_2$H$^+$ abundance decreases more rapidly when it fronts onto strong 20 cm continuum emission. The other abundance ratios, however, do not show obvious an trend as the 20 cm continuum emission flux decreases.

For source 40, the 20 cm continuum emission flux has a positively proportional correlation with the H$_2$ column density, although the correlation is not obvious (in Figure 11 online, we show the 20 cm continuum emission flux as a function of the H$_2$ column density for 51 sources). Considering that abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC have an inversely proportional correlation with the H$_2$ column density, the abundance variations of these four molecules with the 20 cm continuum emission could also be attributed to the variation of the H$_2$ column density to a great extent.

4.5.2. The Second Type

For the second type of sources, the abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC increase as a function of the increasing...
20 cm continuum emission flux (see Table 6). We show source 34 as an example in Figure 8. By checking the abundance distributions of these four molecules in Figure 3 online and 20 cm continuum emission in Figure 9 online, we found that the abundances of these molecules are usually small at the center of the clump, and are large at the edges of the clump, but...
are much larger in the eastern edge of the clump, which fronts onto the 20 cm continuum emission.

Figure 10 displays the abundance ratios as a function of the 20 cm continuum emission flux, where abundance ratios of \( \text{N}_2\text{H}^+ / \text{HCN} \) and \( \text{HCO}^+ / \text{HCN} \) show a weak increasing trend as the 20 cm continuum emission flux decreases. The results suggest that the HCN abundance increases more rapidly than \( \text{N}_2\text{H}^+ \) and \( \text{HCO}^+ \) do. When 20 cm continuum emission becomes strong, \( \text{N}_2\text{H}^+ / \text{HNC} \) also displays a very weak increasing trend as the 20 cm continuum emission flux decreases. This indicates that the HNC abundance decreases more rapidly than \( \text{N}_2\text{H}^+ \) does when 20 cm continuum emission becomes strong. The other three abundance ratios show no obvious variation as a function of the 20 cm continuum emission flux.

For source 34, the 20 cm continuum emission flux shows an inversely proportional correlation with the \( \text{H}_2 \) column density (see Figure 11 online). Considering that abundances of \( \text{N}_3\text{H}^+ \), \( \text{HCO}^+ \), HCN, and HNC have an inverse correlation with the \( \text{H}_2 \) column density, the abundance variations of these four molecules should be positively proportional with the 20 cm continuum emission. Their variations with the 20 cm continuum emission are much larger in the eastern edge of the clump, which fronts onto the 20 cm continuum emission.

Table 6

We Classified 51 Sources Associated with the 20 cm Continuum Emission into Four Types (see Table 1)

| Type      | Abundance with 20 cm Continuum Emission |
|-----------|-----------------------------------------|
| First     | Decreasing                               |
| Second    | Increasing                               |
| Third     | Decreasing (≥10 mJy/beam)               |
| Fourth    | Increasing (≤10 mJy/beam)               |

**Note.** Here we display the trend of abundances with the 20 cm continuum emission for the four types of sources.

Figure 9. The distributions of 20 cm continuum emission for source 40 (G353.198+0.927). The unit of the gray scale bar is mJy/beam. The rms noise is \( \sigma \sim 0.5 \text{ mJy/beam} \). The lower limit for the source is \( 3\sigma \sim 1.5 \text{ mJy/beam} \). This source is an example of the first type; it belongs to Group II. (The complete figure set (51 images) is available.)
continuum emission in this case could also be attributed to the variation of the H$_2$ column density to a great extent. However, the correlation between the 20 cm continuum emission and the abundance is not a simple reverse of the correlation between the 20 cm continuum emission and the H$_2$ column density. This indicates that the environment, such as UV radiation traced by Figure 10.

The abundance ratios between N$_2$H$^+$, HCO$^+$, HCN, and HNC as a function of the 20 cm continuum emission flux for source 40 (G357.198+0.927, an example of the first type, belongs to Group II), source 34 (G352.684-0.120, an example of the second type, belongs to Group I), and source 29 (351.040-0.336, an example of the third type, belongs to Group II) in log-log, respectively.

(The complete figure set (51 images) is available.)
continuum emission, may contribute to the abundance variations of these four molecules. More works based on chemical model are needed to confirm this.

### 4.5.3. The Third Type

We noted that the 20 cm continuum emission flux of the second type of sources is much smaller than that of the first type of sources. This suggests that the abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC have an inversely proportional correlation with the 20 cm continuum emission flux when it is very strong and have a positively proportional correlation with the 20 cm continuum emission flux when it is weak.

As for the third type of sources, the abundances of N$_2$H$^+$, HCO$^+$, HCN, and HNC increase as a function of the 20 cm continuum emission flux when it is less than a certain value and decrease as a function of the 20 cm continuum emission flux when it is greater than the same value (see Table 6). We show source 29 as an example in Figure 8. When the 20 cm continuum emission flux is greater than \( \approx 10 \text{ mJy/beam} \), HCO$^+$, HCN, and HNC abundances display an obvious increasing trend as the 20 cm continuum emission flux decreases. When the 20 cm continuum emission flux is less than \( \approx 10 \text{ mJy/beam} \), these abundances display a weak increasing trend as the 20 cm continuum emission flux increases. The three-color image of the source indicates that new stars are being formed in its center (Figure 2 online), and the 20 cm continuum emission is stronger in the northern part of the clump (Figure 9 online). N$_2$H$^+$, HCO$^+$, HCN, and HNC abundances are small in the central part of the clump and in the eastern and southern edges (see Figure 3 online). These results show that abundances are large in pixels where 20 cm continuum emission is relatively strong and the column density is relatively low. N$_2$H$^+$ abundance displays a similar trend of variation when 20 cm continuum emission flux is greater or less than \( \approx 10 \text{ mJy/beam} \), but the dispersion is larger.

The abundance ratios of N$_2$H$^+$/HCN, N$_2$H$^+$/HCO$^+$, and N$_2$H$^+$/HNC display a weak increasing trend as a function of the increasing 20 cm continuum emission flux (see Figure 10), and so abundances of HCN, HCO$^+$ and HNC increase more slowly as a function of 20 cm continuum emission than N$_2$H$^+$ does. The fact that abundance ratios of HCN/HNC, HCO$^+$/HCN, and HCO$^+$/HNC show no obvious trend as a
function of 20 cm continuum emission indicates the abundances of HCN, HCO\(^+\), and HNC vary at a similar rate in this case.

For source 29, the 20 cm continuum emission flux shows a positively proportional correlation with the H\(_2\) column density when it is greater than 10 mJy/beam and shows an inversely proportional correlation with the H\(_2\) column density when it is less than 10 mJy/beam (see Figure 11 online). This is contrary to the abundance variations (Figure 8). Based on the same consideration as that for sources 40 and 34, the abundance variations of N\(_2\)H\(^+\), HCO\(^+\), HCN, and HNC with the 20 cm continuum emission could also be attributed to the variation of the H\(_2\) column density to a great extent.

Considering that 20 cm continuum emission is positively correlated with the UV radiation of nearby OB stars, it is natural to predict that the 20 cm continuum emission is correlated with the spatial variations of the abundance of N\(_2\)H\(^+\), HCO\(^+\), HCN, and HNC. However, the abundance variations are likely to be a more complex function of environment and radiative transfer (i.e., a combination of opacity, excitation, and radiation field; Schap et al. 2017). This may explain the reason for which we did not see obvious correlation between 20 cm continuum emission and molecule abundances for many sources, which we described as the fourth type sources (see Tables 1 and 6).

Briefly, we found good correlations between the molecules’ abundances and 20 cm continuum emission in the first, second, and third types of sources, which could also be attributed to the variation of the H\(_2\) column density. We did not find obvious correlations between the abundance ratios and 20 cm continuum emission.

5. Conclusions

We derived the distribution of abundances of N\(_2\)H\(^+\), HCO\(^+\), HCN, HNC, and abundance ratios between them and studied their spatial variations and correlations with the H\(_2\) column density, temperature, and 20 cm continuum emission. Our main conclusions are as follows.

1. We derived the distribution of the temperature; the H\(_2\) column density; abundances of N\(_2\)H\(^+\), HCO\(^+\), HCN, and HNC; and the abundance ratio between them for 90 massive star-forming clumps.
2. The abundances of N\(_2\)H\(^+\), HCO\(^+\), HCN, and HNC increase as a function of the decreasing column density and increasing temperature. This reason for the seems to be that these molecules are not optically thin. We just detected them in the outer layer of the molecular cloud; while dust emission is optically thin, we thus derived the total H\(_2\) column density along the line of sight. The column densities of these four molecules vary little when the H\(_2\) column density varies about one order of magnitude. So the spatial variations of the abundances of these four molecules were dominated by the H\(_2\) column density.
3. The abundance ratios between N\(_3\)H\(^+\), HCO\(^+\), HCN, and HNC also display systemic variations as a function of the column density. This could be explained by the chemical properties of these four molecules. However, for the sources that overlapped with bubbles, the abundance ratios between these molecules usually show no obvious trend as a function of the column density and temperature. This may be attributed to the effect from the environment.
4. For the sources where the 20 cm continuum emission is very strong, the abundances of these four molecules decrease as a function of the increasing 20 cm continuum emission flux. However, for the sources where the 20 cm continuum emission flux is weak, the abundances of these four molecules increase as a function of the increasing 20 cm continuum emission flux. These variations are mainly dominated by the H\(_2\) column density.
5. The 20 cm continuum emission is correlated with the UV radiation of OB stars nearby, and so it is probably associated with the spatial abundance variations of the molecules. However, the abundance ratios between these four molecules usually do not show an obvious trend as a function of the 20 cm continuum emission flux. This suggests that the effect from the environment traced by 20 cm continuum emission does not affect the abundance too much.
6. The spatial variations of the abundances of N\(_2\)H\(^+\), HCO\(^+\), HCN, and HNC are dominated by the H\(_2\) column density, and massive stars form in clumps by the cluster. As the result, obvious column density variation exists in massive star-forming regions and, therefore, obvious spatial variations of chemical properties. It is difficult to extract the chemical properties that characterize the evolution of massive star-forming regions.

Noted that we use simple approaches to estimate the abundances, such as assuming a fixed excitation temperature and assuming the local dust temperature to be the gas excitation temperature. In fact, abundance variations are likely to be a more complex function of the environment and radiative transfer (i.e., a combination of opacity, excitation, and radiation field; Schap et al. 2017). So more work based on chemical models and optical molecular lines is needed.

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