Cyanopolyyne Chemistry around Massive Young Stellar Objects

Kotomi Taniguchi1,2,6, Eric Herbst1,2, Paola Caselli3, Alec Paulive2, Dominique M. Maffucci2, and Masao Saito4,5

1 Department of Astronomy, University of Virginia, Charlottesville, VA 22904, USA; kt8pm@virginia.edu
2 Department of Chemistry, University of Virginia, Charlottesville, VA 22903, USA
3 Max-Planck-Institute for Extraterrestrial Physics (MPE), Giessenbachstr, 1, D-85748 Garching, Germany
4 Department of Astronomical Science, School of Physical Science, SOKENDAI (The Graduate University for Advanced Studies), Osawa, Mitaka, Tokyo 181-8588, Japan
5 Department of Astronomy, University of Virginia, Charlottesville, VA 22904, USA; kotomi.taniguchi@niras.kyoto-u.ac.jp

Received 2019 February 26; revised 2019 June 18; accepted 2019 June 26; published 2019 August 13

Abstract

Recent radio astronomical observations have revealed that HC$_3$N, the second shortest cyanopolyyne (HC$_{2n+1}$N), is abundant around some massive young stellar objects (MYSOs), which is not predicted by classical carbon-chain chemistry. For example, the observed HC$_3$N abundance toward the G28.28–0.36 MYSO is higher than that in L1527, which is one of the warm carbon-chain chemistry sources, by more than one order of magnitude. In this paper, we present chemical simulations of hot-core models with a warm-up period using the astrochemical code Nautilus. We find that the cyanopolyynes are formed initially in the gas phase and accreted onto the bulk and surface of granular ice mantles during the lukewarm phase, which occurs at 25 < $T$ < 100 K. In slow warm-up period models, the peak abundances occur as the cyanopolyynes desorb from dust grains after the temperature rises above 100 K. The lower limits of the abundances of HC$_3$N, CH$_3$CCH, and CH$_3$OH observed in the G28.28–0.36 MYSO can be reproduced in our hot-core models, after their desorption from dust grains. Moreover, previous observations suggested chemical diversity in envelopes around different MYSOs. We discuss possible interpretations of relationships between stages of the star formation process and such chemical diversity, such as the different warm-up timescales. This timescale depends not only on the mass of central stars but also on the relationship between the size of warm regions and their infall velocity.

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

1. Introduction

Knowledge of the chemical composition allows us to use molecules as powerful diagnostic tools of the physical conditions and dynamical evolution of star-forming regions (e.g., Caselli & Ceccarelli 2012; van Dishoeck 2018). Recent improvements in efficiencies of radio telescopes enable the achievement of high sensitivities with high angular resolution within reasonable observing times. Owing to such developments, we can detect molecules with abundances significantly lower than previously detected species (e.g., McGuire et al. 2018), including isotopologues (Taniguchi et al. 2016a; Taniguchi & Saito 2017; Burkhardt et al. 2018). The discovery of these molecules in various evolutionary stages raises new challenges in the fields of chemical network simulation and laboratory experiment.

Unsaturated carbon-chain species, such as C$_{2n}$H, CCS, and the cyanopolyynes (HC$_{2n+1}$N), are unique molecules in the interstellar medium. For a long time, they have been thought to be abundant in young starless cores and decrease in abundance in later stages of low-mass star formation (Benson et al. 1998; Hirota et al. 2009; Suzuki et al. 1992). The precursors of carbon-chain molecules in starless cores are mainly ionic carbon (C$^+$) and atomic carbon (C). Carbon-chain molecules are mainly formed via gas-phase ion-molecule reactions and neutral–neutral reactions, the reaction rate coefficients, of which can be large even at low temperatures such as $T$ $\approx$ 10 K.

In contrast to the above classical picture, low-mass protostellar cores rich in carbon-chain species have been found in sources such as L1527 in Taurus (Sakai et al. 2008) and IRAS15398–3359 in Lupus (Sakai et al. 2009). On the other hand, saturated complex organic molecules have been found to be abundant around protostars (Herbst & van Dishoeck 2009) in so-called hot cores and hot corinos in high- and low-mass star-forming regions, respectively. Therefore, the discovery of such low-mass protostellar cores rich in carbon-chain species was surprising initially. The chemistry that produces these species was named “warm carbon-chain chemistry” (WCCC; Sakai & Yamamoto 2013). In WCCC, the formation of carbon-chain molecules starts with the desorption of CH$_3$ from dust grains at a temperature of $\sim$25 K. The reaction between CH$_3$ and C$^+$ and subsequent gas-phase reactions then lead to the formation of carbon chains (Hassel et al. 2008). The different timescale of prestellar collapse was proposed as an origin of the difference between WCCC and hot corino chemistry (Sakai & Yamamoto 2013); the short and long starless core phases lead to WCCC and hot corino sources, respectively. On the other hand, Spezzano et al. (2016) suggested that different illumination by the interstellar radiation field around dense cloud cores could produce such chemical differentiation, based on their observations toward the L1544 prestellar core. Hence, the origin of the chemical diversity found in low-mass star-forming regions is still controversial.

Observational studies of carbon-chain molecules in high-mass star-forming regions tend to be less detailed than those of low-mass star-forming regions. Nevertheless, cyanopolyynes have been detected in some famous high-mass star-forming regions such as Sgr B2 (Belloche et al. 2013; Bonfand et al. 2017) and the Orion regions, Orion KL (Esplugues et al. 2013), and OMC-2 FIR4 (Fontani et al. 2017). Survey observations of HC$_3$N and HC$_5$N have been conducted toward high-mass starless cores (HMSCs) and high-mass protostellar
objects (HMPOs) using the Nobeyama 45 m radio telescope (Taniguchi et al. 2018c, 2019). This group detected HC$_5$N in almost all of the target sources and detected HC$_3$N in half of the HMPOs. Indeed, HC$_5$N seems to be ubiquitous around HMPOs. Taniguchi et al. (2017) found that HC$_5$N is abundant in envelopes around three massive young stellar objects (MYSOs) associated with the 6.7 GHz methanol masers using the Green Bank 100 m and Nobeyama 45 m telescopes. The HC$_5$N abundance in G28.28−0.36, which is one of the target MYSOs, is higher than that in the Class 0 protostar L1527 by a factor of 20. In addition, Taniguchi et al. (2018b) suggested chemical diversity around MYSOs as a reason for the varying cyanopolyne abundances; organic-poor MYSOs are surrounded by a cyanopolyne-rich lukewarm envelope, while organic-rich MYSOs, namely hot cores, are surrounded by a CH$_3$OH-rich lukewarm envelope.

In this paper, we report an investigation of the cyanopolyne chemistry using hot-core models with a warm-up period, motivated by the particularly high abundance of HC$_5$N in the G28.28−0.36 MYSO. Cyanopolyynes are relatively stable species compared with other carbon-chain species and can survive in high temperature regions (Hassel et al. 2011). In fact, the vibrationally excited lines of HC$_5$N and the extremely high-J rotational lines of HC$_3$N have been detected in Sgr B2(N) and Orion KL (Espagne et al. 2013; Bonfand et al. 2017). In addition, HC$_5$N and HC$_3$N were detected in a candidate position of the molecular outflow around G28.28−0.36 (Taniguchi et al. 2018a). Therefore, there is a large possibility that cyanopolyynes exist in hot-core regions, where the temperature is higher than in WCCC sources, and where formation mechanisms of cyanopolyynes may differ in the two types of regions. Furthermore, the formation paths of cyanopolyynes have been thought to consist of possible steps in the synthesis of prebiotic molecules (Jaber Al-Edhari et al. 2017), so it is also important to reveal their formation paths for science related to the origins of life.

In Section 2, we describe our models, with results found in Section 3. We compare models, and the model results with the observational results around MYSOs (Taniguchi et al. 2017, 2018b) in Sections 4.1 and 4.2, respectively. Effects of the cosmic-ray ionization rate on the HC$_5$N abundance are investigated in Section 4.3. The chemistry of cyanopolyynes is compared with that of other carbon-chain species during the warm-up period in Section 4.4. Possible origins of the chemical diversity around MYSOs are discussed in Section 4.5. Finally, our conclusions are presented in Section 5.

### 2. Models

In this study, we used the gas-grain Nautilus code (Ruaud et al. 2016) supplemented by preliminary reactions involving irradiation (Shingledecker & Herbst 2018) to model the freefall collapse and warm-up periods of hot-core evolution (Garrod & Herbst 2006). We ran both the three-phase model, in which the chemistry of the grain surface and the bulk ice are distinguished, and the two-phase model, in which the grain surface and bulk ice are not distinguished (Ruaud et al. 2016). The cosmic-ray ionization rate was assumed to be $1.3 \times 10^{-17}$ s$^{-1}$. The ratio between diffusion energy and binding energy was set at 0.5 (Garrod & Herbst 2006). The binding energies of major species and key species in the following sections are summarized in the Appendix. The competitive mechanism was used for surface reactions with chemical activation energy (Herbst & Millar 2008). Table 1 lists the initial elemental abundances with respect to total hydrogen. These elemental abundances correspond to the low-metal abundances, which are typically used for modeling the chemistry of dark clouds. We assume that all of the hydrogen is in the form of H$_2$ at the initial stage. There are 7646 gas-phase reactions and 498 gas-phase species, mainly taken from the Kinetic Database for Astrochemistry (KIDA). $^7$We also included data taken from Balucani et al. (2015) and Skouteris et al. (2018). Balucani et al. (2015) proposed new reactions forming methyl formate and dimethyl ether. Skouteris et al. (2018) studied a new scheme for the synthesis of glycolaldehyde, acetic acid, and formic acid. There are 5323 grain-surface reactions and 431 grain-surface species including suprathermal species (Shingledecker & Herbst 2018). The surface reactions come mainly from Garrod (2013), with additional data taken from Bergantini et al. (2018) and Hudson & Moore (2018). The reactions between CH$_3$OH and CH$_2$ (the asterisk mark *) means the suprathermal species; Bergantini et al. (2018) and between CH$_3$CO and CH$_3$ including suprathermal species (Hudson & Moore 2018; Shingledecker & Herbst 2018) are included. The self-shielding effects of H$_2$ (Lee et al. 1996), CO (Visser et al. 2009), and N$_2$ (Li et al. 2013) are included.

In addition to the self-shielding effects, Nautilus allows for variation of different parameters through switches. Included switches are as follows: enhancement of H$_2$ grain formation (off); enabling of photodesorption of ices (on); inclusion of cosmic-ray diffusion (on);$^8$ inclusion of Eley–Rideal mechanism (off); enabling of radiolysis (off). In our reaction network, reactions between cyanopolyynes and radicals on dust surface, which lead to destruction of cyanopolyynes, are not included. Since few of these processes have been studied to the best of our knowledge, and since theoretical treatments are not readily available, we did not try to add such reactions to our network. As shown in the following sections, cyanopolyynes in the gas-phase are destroyed mainly by atomic and molecular ions, which are not included in the dust surface and ice mantles: all dust-surface and ice-mantle species are neutral. One neutral species, which can destroy the cyanopolyynes, is neutral atomic

| Element | Abundance |
|---------|-----------|
| H$_2$   | 0.5       |
| He      | 0.09      |
| C$^+$   | $7.3 \times 10^{-5}$ |
| N       | $2.14 \times 10^{-5}$ |
| O       | $1.76 \times 10^{-4}$ |
| F       | $1.8 \times 10^{-8}$ |
| Si$^+$  | $8 \times 10^{-9}$ |
| S$^+$   | $8 \times 10^{-8}$ |
| Fe$^+$  | $3 \times 10^{-9}$ |
| Na$^+$  | $2 \times 10^{-9}$ |
| Mg$^+$  | $7 \times 10^{-9}$ |
| Cl$^+$  | $1 \times 10^{-7}$ |
| P$^+$   | $2 \times 10^{-10}$ |

Note. Taken from the AL model in Acharyya & Herbst (2017).

---

$^7$ [http://kida.obs.uj-bordeaux1.fr](http://kida.obs.uj-bordeaux1.fr)

$^8$ The effect of cosmic ray impacts, which cause a stochastic heating of the dust particles allowing for surface radicals to diffuse quickly and react to form more complex species (Reboussin et al. 2014).
carbon, but its abundance on dust surfaces is rather low due to rapid hydrogenation reactions even at low temperatures.

We adopted the physical evolution of the two-stage hot-core model described by Garrod & Herbst (2006). The first stage corresponds to the freefall collapse period. The initial gas density is \( n_H = 10^4 \text{ cm}^{-3} \) and increases to \( 10^7 \text{ cm}^{-3} \) during the freefall collapse, which lasts for \( \sim 5 \times 10^5 \text{ yr} \), while the visual extinction \( (A_V) \) increases from 5 mag to over 500 mag according to the increase in \( n_H \). The temperature is kept constant at 10 K (Garrod & Herbst 2006).

The second stage is the warm-up period, during which the temperature rises from 10 K to 200 K according to the following formula (Garrod & Herbst 2006):

\[
T = T_0 + (T_{\text{max}} - T_0) \left( \frac{\Delta t}{t_h} \right)^n,
\]

where \( T_0 \), \( T_{\text{max}} \), \( t_h \), and \( n \) are the initial temperature (10 K), the maximum temperature (200 K), the heating timescale, and the order of the heating, respectively. We chose \( n = 2 \), following Hassel et al. (2008). Three heating timescales were adopted: \( 5 \times 10^4 \text{ yr} \) (Fast), \( 2 \times 10^5 \text{ yr} \) (Medium), and \( 1 \times 10^6 \text{ yr} \) (Slow), approximating high-mass, intermediate-mass, and low-mass star formation, respectively (Viti et al. 2004). The dust temperature is assumed to be equal to the gas temperature. Figure 1 shows the time variation of temperature, \( H_2 \) density, and visual extinction. After the final temperature of 200 K is reached, the system remains at this temperature, at which chemistry can still occur. In practice, several dynamical changes such as the molecular outflow and disk formation occur, but our models do not include the effects from these phenomena. Table 2 summarizes the models utilized.

### Table 2

| Model | \( t_h \) \(^a\) | Phase   |
|-------|-----------------|---------|
| M1    | Fast            | 3-phase |
| M2    | Medium          | 3-phase |
| M3    | Slow            | 3-phase |
| M4    | Fast            | 2-phase |
| M5    | Medium          | 2-phase |
| M6    | Slow            | 2-phase |

Note.

\(^a\) Fast, Medium, and Slow correspond to \( 5 \times 10^4, 2 \times 10^5, \) and \( 1 \times 10^6 \text{ yr} \), respectively.

3. Results

#### 3.1. Cyanopolyne Chemistry during the Freefall Collapse Period

Figure 2 shows the abundances of \( HC_3N \), \( HC_5N \), and \( HC_7N \) in the gas phase during the freefall collapse period. The abundances of \( HC_3N \) and \( HC_5N \) at timescales of \( 5 \times 10^3 - 4 \times 10^5 \text{ yr} \) agree with the abundances observed in HMSCs \( (X(HC_3N) \sim 10^{-11} - 10^{-10}) \) and \( X(HC_5N) \sim 10^{-12} - 10^{-11}; \) Taniguchi et al. 2018c). HMSCs typically have gas densities of order \( 10^4 \text{ cm}^{-3} \) at fractions of a parsec (Beuther et al. 2002). Therefore, the results during the freefall collapse period seem to be reasonable.
During the freefall collapse stage, the following reaction significantly contributes to the formation of HC$_3$N:

$$\text{N} + \text{C}_4\text{H} \rightarrow \text{HC}_3\text{N} + \text{C.}$$  \hfill (2)

After an interval of $6 \times 10^3$ yr, HC$_3$N is also formed significantly by the dissociative recombination reaction

$$\text{HC}_3\text{NH}^+ + e^- \rightarrow \text{HC}_3\text{N} + \text{H.}$$  \hfill (3)

Several reactions contribute to the formation of HC$_5$N and HC$_7$N, and their fraction changes with time. The following types of reactions largely form these species:

$$\text{H}_2\text{C}_n\text{N}^+ + e^- \rightarrow \text{HC}_n\text{N} + \text{H},$$  \hfill (4)

$$\text{N} + \text{C}_n\text{H}^- \rightarrow \text{HC}_n\text{N} + e^-,$$  \hfill (5)

and

$$\text{N} + \text{C}_{n+1}\text{H} \rightarrow \text{HC}_n\text{N} + \text{C},$$  \hfill (6)

where $n = 5, 7$.

Cyanopolyynes are mainly destroyed by reactions with C$^+$ before $5 \times 10^3$ yr and reactions with C between $5 \times 10^3$ and $2 \times 10^5$ yr:

$$\text{HC}_n\text{N} + \text{C}^+ \rightarrow \text{H} + \text{C}_{n+1}\text{N}^+,$$  \hfill (7)

$$\text{HC}_n\text{N} + \text{C}^+ \rightarrow \text{CN} + \text{C}_n\text{H}^+,$$  \hfill (8)

and

$$\text{HC}_n\text{N} + \text{C} \rightarrow \text{H} + \text{C}_{n+1}\text{N},$$  \hfill (9)

where $n = 3, 5, 7$.

### 3.2. Cyanopolyne Chemistry during the Warm-up Period

Figure 3 shows cyanopolyne abundances in the gas phase, dust surface, and bulk of the icy mantle during the warm-up period for the slow, three-phase model M3. The zero of time is the starting time of the model calculation in the freefall collapse stage. The left-hand side of each abscissa corresponds to the start of the warm-up period, at around $5 \times 10^3$ yr. Note that the temperature is followed with time by a black dashed line. The formation mechanisms of cyanopolyynes are basically the same in all of the models, depending on the temperature. We use Model M3 because we can investigate the temperature dependence of cyanopolyne chemistry during the warm-up period in the most detail.

#### 3.2.1. HC$_3$N

The HC$_3$N abundance, especially in the gas phase, begins an increase around $t = 7 \times 10^3$ yr when the temperature reaches 25 K and the WCCC chemistry onsets (Sakai & Yamamoto 2013). Figure 4 shows the CH$_4$ abundances in the gas phase, dust surface, and bulk of the icy mantle of Models M3 and M6. The gas-phase CH$_4$ abundance steeply increases and the abundances in dust surface and ice mantles decrease at
The increases in the gas phase values of CN and C2H2 lead to abundance increases because of its desorption from dust grains. 

\[
CH_4 + C \rightarrow C_2H_2 + H, \quad (11)
\]

The species HC3N formed in the gas phase is partially accreted into the bulk of the icy mantle, as is the case for HC5N. At \( t = 1.2 \times 10^5 \) yr \( (T \approx 94 \) K), HC2N is desorbed into the gas, and reaches its peak abundance. This abundance corresponds to that in the bulk of the mantle, right before desorption, as shown in panel (b) of Figure 3, in a similar manner to HC3N. The subsequent decrease is caused by reaction with HCO+ and other protonated ions.

\[
CCH + HC_3N \rightarrow HC_5N + H. \quad (13)
\]

After the temperature reaches 25 K, HC3N is efficiently formed by the following reaction:

\[
C_5H_2 + CN \rightarrow HC_5N + H. \quad (14)
\]

The C5H2 species is formed by the reaction between C2H2 and C6H, which is similar to Reaction (12). In addition, gaseous C5H2 reaches its peak abundance just after its direct sublimation from dust grains at \( t = 1.2 \times 10^5 \) yr \( (T \approx 94 \) K) and the reaction rate of Reaction (14) increases. This leads to an increase in the HC5N abundance. The HC5N species is also produced by the reaction

\[
CCH + HC_5N \rightarrow HC_7N + H. \quad (15)
\]

At these low temperatures, HC3N formed in the gas phase is partially depleted onto dust grains following each enhancement and accumulates in the bulk of the icy mantle. The result is a pattern for the HC3N abundance versus time that resembles a spectrum. At \( t \approx 1.1 \times 10^5 \) yr \( (T \approx 90 \) K), HC3N sublimates from dust grains and reaches its peak abundance in the gas phase. The peak abundance in the gas phase is consistent with that of the bulk of the icy mantle, as shown in panel (a) of Figure 3.

\[
3.2.2. \text{HC}_3\text{N}
\]

HC3N is mainly formed by the following reaction in the warming gas \( (T > 25 \) K):

\[
C_2H_2 + CN \rightarrow HC_3N + H, \quad (11)
\]

while the precursor C2H2 is produced by the reaction

\[
\text{CCH} + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_2 + \text{H}, \quad (12)
\]

and the radical CCH is formed by the electron recombination reaction of C2H+. The ion C2H+ is formed by the reaction between CH4 and C+, as discussed in the preceding section. The gas-phase species C4H2 sharply increases at \( t = 1.0 \times 10^5 \) yr \( (T \approx 73 \) K) via its direct sublimation from dust grains. Owing to increases in the C4H2 abundance, Reaction (11) is enhanced, leading to an increase in the HC5N abundance. The radical CCH also reacts with HC3N in the gas phase to produce HC5N by the reaction

\[
\text{CCH} + \text{HC}_3\text{N} \rightarrow \text{HC}_5\text{N} + \text{H}. \quad (13)
\]

\[
\text{HC}_3\text{N} + \text{HCO}^+ \rightarrow \text{HC}_5\text{N} + \text{CO}, \quad (16)
\]

where \( n = 3, 5, 7 \).

The peak abundance of HC3N is higher than that of HC5N, which may not be realistic. Occasionally the largest species in a sequence, such as HC3N (if it is truly the largest) is not described well in a network. The high HC3N abundance may reflect that there are unknown important destruction reactions of cyanopolyynes both in the gas phase and dust surface. For example, radicals can move on dust grains during the warm-up period and reactions between cyanopolyynes and radicals may decrease the abundances of cyanopolyynes on dust surface and ice mantles. However, our current reaction networks do not contain such reactions, while photodissociation destruction processes are included. Besides photodissociation processes, if other destruction reactions of cyanopolyynes on dust surface exist, the longer cyanopolyynes will be more affected because longer cyanopolyynes stay for a longer time due to higher sublimation temperatures in our current model.
In summary, the cyanopolyynes are produced by a combination of neutral–neutral and ion–neutral gas-phase reactions during the warm-up period \((T > 25 \text{ K})\) and accumulate on and in the dust mantles before the temperature reaches their sublimation temperatures. The sublimation of first CN and second the \(\text{C}_2\text{H}_2\) \((n = 1, 2, 3)\) species enhances key reactions to form the cyanopolyynes, which partly accrete onto dust mantles. As the temperature rises, the pattern of enhancements in the production of the gaseous cyanopolyynes followed by partial accretion onto grains leads to a characteristic spectral-type pattern. When the temperature rises past the sublimation temperatures of cyanopolyynes, they desorb into the gas, and reach their peak abundances. The spectral-type abundance profile is best seen in the slow models, but exists to a lesser extent in the faster models too. Cyanopolyynes are mainly destroyed by reactions with HCO\(^+\) and other protonated ions in the gas phase and their abundances decrease.

4. Discussion

4.1. Comparisons of Cyanopolyyne Abundances among Models

Figure 5 shows comparisons of the cyanopolyyne abundances in the gas-phase during the warm-up period, among all models, while Table 3 summarizes the peak abundances during the warm-up and hot-core periods of cyanopolyynes in the gas phase and the corresponding temperatures in each model. In the fast and medium warm-up models (red and green lines), cyanopolyynes reach higher abundances in the gas phase after their desorption. Given the rapidity of desorption, their peak abundances do not correspond to their abundances on the dust...
surface or bulk of the icy mantle during the desorption. The post-desorption syntheses in the gas phase are particularly important for the longer chains. One possible reason for their importance is that there is not enough time to accumulate on dust surfaces or in the bulk of the icy mantles during the short heating timescale. On the other hand, accumulation on the dust surface and in the bulk of the icy mantle play essential roles in producing the high cyanopolyne abundances during the warm-up period when there is enough time for cyanopolynones to adsorb onto dust grains. This seems to depend on the assumed initial density.

When we compare the peak abundances in Model M3 (slow; 3-phase) with those in Model M6 (slow, 2-phase), we find that the peak abundances in M3 are higher by a factor of 2–8, as shown in Table 3. These different peak abundances between Models M3 and M6 support the hypothesis that accumulation of cyanopolynones in the bulk of the icy mantle enhances their abundances in the gas phase after their desorption at higher temperatures, because, basically, the ice prevents the gas phase destruction of cyanopolynones by maintaining their peak abundances unaltered in the mantles.

### 4.2. Comparisons with Observations

Table 4 contains summaries of the observed abundances of HC$_5$N, CH$_3$CCH, and CH$_3$OH in three MYSOs (Taniguchi et al. 2017, 2018b) and the peak calculated abundances in each model. We excluded HC$_5$N because its column densities and excitation temperatures in the observed MYSOs seem to include large uncertainties (Taniguchi et al. 2018b). These observations were carried out using single-dish telescopes and thus, because of beam dilution, the derived abundances and rotational temperatures are lower limits (Taniguchi et al. 2017). Hence, our criterion for reproduction is that the model produces more than the observed lower limit in the following sections.

We found that the maximum model abundances of the three gas-phase species are higher than the observed lower limits in all of the models. We also derived their abundances in L1527, a low-mass WCCC source, and found, once again that the model peak abundances exceed the observed lower limits.

We are particularly interested in G28.28—0.36, because this source shows a uniquely high HC$_5$N/CH$_3$OH feature, discussed below, among the observed sources (Taniguchi et al. 2018b). In addition, G28.28—0.36 shows a relatively high HC$_5$N abundance, as derived with the single-dish observations (Taniguchi et al. 2017). In the Orion KL hot core, the HC$_5$N abundance with respect to H$_2$ was derived to be 1.7 × 10$^{-10}$ (Esplugues et al. 2013). Therefore, the HC$_5$N abundance in G28.28—0.36 is higher than that in the Orion KL hot core by more than one order of magnitude. As already mentioned in Section 1, the HC$_5$N abundance in G28.28—0.36 is higher than that in L1527 by a factor of 20, as shown in Table 4. The particularly high HC$_5$N abundance in G28.28—0.36 cannot be explained by WCCC in the lukewarm envelope ($T \sim 20$–30 K, Hassel et al. 2008, 2011).

We now compare our model results with the lower limits of HC$_5$N, CH$_3$CCH, and CH$_3$OH in G28.28—0.36 in order to constrain the minimum temperatures in the warm-up period where they reside. Figure 6 shows the model results with the lower limits to molecular abundances in G28.28—0.36 as

---

### Table 3

The Peak Calculated Abundances of Cyanopolynones in the Gas Phase and the Corresponding Temperature

| Model | HC$_5$N Abundance | T (K) | HC$_5$N Abundance | T (K) | HC$_5$N Abundance | T (K) |
|-------|-------------------|------|-------------------|------|-------------------|------|
| M1    | 3.62 × 10$^{-8}$  | 200  | 1.08 × 10$^{-7}$  | 200  | 6.03 × 10$^{-8}$  | 200  |
| M2    | 2.79 × 10$^{-8}$  | 200  | 7.66 × 10$^{-8}$  | 200  | 6.20 × 10$^{-8}$  | 200  |
| M3    | 4.39 × 10$^{-8}$  | 98   | 1.14 × 10$^{-7}$  | 129  | 5.19 × 10$^{-9}$  | 162  |
| M4    | 1.98 × 10$^{-8}$  | 200  | 8.97 × 10$^{-8}$  | 200  | 6.41 × 10$^{-8}$  | 200  |
| M5    | 2.15 × 10$^{-8}$  | 96   | 4.42 × 10$^{-8}$  | 200  | 1.45 × 10$^{-8}$  | 200  |
| M6    | 1.11 × 10$^{-8}$  | 92   | 5.02 × 10$^{-8}$  | 129  | 6.44 × 10$^{-10}$ | 162  |

### Table 4

Lower Limits of Observed Abundances in MYSOs and the Peak Calculated Abundances of HC$_5$N, CH$_3$CCH, and CH$_3$OH

| Source/Model | HC$_5$N (× 10$^{-7}$) | CH$_3$CCH (× 10$^{-7}$) | CH$_3$OH (× 10$^{-7}$) |
|--------------|------------------------|--------------------------|-------------------------|
| G12.89+0.49  | (2.1 +1.5 _1.1_1.9)  | (1.9 +1.4 _1.1_1.9)    | (1.0 +0.5_1.0_1.0)     |
| G16.86-2.16  | (8.0 +3.5_2.3_2.8)    | (1.6 +0.9_0.7_0.9)     | (4.4 +3.5_3.1_3.4)     |
| G28.28-0.36  | (2.1 +1.3_1.1_1.9)    | (3.8 +2.2_1.6_1.8)     | (2.3 +1.7_1.3_1.6)     |
| L1527 (WCCC) | (1.2 +0.3_0.5_0.6)    | (1.07 ± 0.05_0.05_0.07) | (1.1 ± 0.2_0.1_0.1)    |

Notes.

1. Abundances taken from Taniguchi et al. (2017, 2018b) and converted to abundances with respect to total hydrogen.
2. Column densities of HC$_5$N, CH$_3$CCH, and CH$_3$OH taken from Sakai & Yamamoto (2013) and (H$_2$) value of 2.8 × 10$^{22}$ cm$^{-2}$ taken from Jørgensen et al. (2002). The abundances with respect to H$_2$ are converted to abundances with respect to total hydrogen.

---

### Notes

- Abundances taken from Taniguchi et al. (2017, 2018b) and converted to abundances with respect to total hydrogen.
- Column densities of HC$_5$N, CH$_3$CCH, and CH$_3$OH taken from Sakai & Yamamoto (2013) and (H$_2$) value of 2.8 × 10$^{22}$ cm$^{-2}$ taken from Jørgensen et al. (2002).
horizontal black dashed lines. Table 5 summarizes the range of ages and lower limits of temperature constrained by the comparisons between the model results and the observed lower limits. The range of ages is determined as the continuous times when the model abundances are higher than the observed lower limits. The observed lower limit of HC$_5$N is reproduced only at ages after it desorbs from dust grains in all the models. Therefore, the chemistry in the lukewarm temperature range of $25 < T < 100$ K cannot explain the high HC$_5$N abundance in G28.28$-$0.36, because its desorption temperature is higher than 100 K. The ages when the temperature reaches the HC$_5$N sublimation temperature of $\sim 115$ K are $5.9 \times 10^5$ yr and $1.2 \times 10^6$ yr in the Medium and Slow warm-up models, respectively. In the Fast warm-up models, further gas-phase formation is needed to reproduce the observed HC$_5$N abundance. Hence, the lower limit of the observed HC$_5$N abundance cannot be reproduced at its sublimation temperature ($t \sim 4.8 \times 10^5$ yr).

The carbon-chain species CH$_3$CCH, shown in the middle panels of Figure 6, is formed in the gas phase during the warm-up period triggered initially by desorption of CH$_4$ via the following reactions:

$$\text{CH}_4 + \text{C}^+ \rightarrow \text{C}_2\text{H}_3^+ + \text{H},$$

(17)

$$\text{CH}_4 + \text{C}_2\text{H}_3^+ \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2,$$

(18)

followed by

$$\text{C}_3\text{H}_5^+ + \text{e}^- \rightarrow \text{CH}_3\text{CCH} + \text{H}.$$  

(19)

The CH$_3$CCH is subsequently adsorbed onto dust grains, in analogy with the cyanopolyyenes, and starts to desorb at a temperature of 70 K. The minimum temperature at which its lower limit observed in G28.28$-$0.36 ($3.8^{+2.6}_{-2.2} \times 10^{-8}$) is
reproduced occurs only after its desorption from dust grains at ≈80 K, corresponding to ages of 4.7 × 10^5 yr, 5.6 × 10^5 yr, and 1.1 × 10^6 yr in the Fast, Medium, and Slow warm-up models, respectively. Its abundances decrease more rapidly compared to those of HC$_5$N, and the ranges of time that can reproduce the observed abundance become narrower. Unlike HC$_5$N, CH$_3$CCH is destroyed by the reaction with atomic oxygen, leading to CO + C$_2$H$_4$. This reaction seems to contribute to the faster destruction of CH$_3$CCH.

The lower panels of Figure 6 show the results for CH$_3$OH, which is not a species produced by WCCC, because its sole production occurs on the grains via hydrogenation of CO. Nevertheless, its lower limit observed in G28.28–0.36 is also reproduced only after it desorbs into the gas phase at temperatures above ∼100 K. The corresponding ages of the CH$_3$OH sublimation are 4.8 × 10^5 yr, 5.8 × 10^5 yr, and 1.1 × 10^6 yr in the Fast, Medium, and Slow warm-up models, respectively. Methanol is destroyed by reactions with ions such as HCO$^+$.

In summary, the lower limits of all of these species derived in G28.28–0.36 can be reproduced only after desorption from dust grains. The observed species in G28.28–0.36 seem to reside in higher temperature regions when compared with WCCC sources. The HC$_5$N and CH$_3$OH abundances do not become higher than the observed abundances at the same age in the Slow warm-up models, although their peaks can be higher than the observed ones at different ages (Table 5).

We now return to a comparison of theory and observation concerning the abundance ratio of HC$_5$N to methanol in G28.28–0.36. The derived N(HC$_5$N)/N(CH$_3$OH) column density ratio in G28.28–0.36 (0.091$^{+0.010}_{-0.035}$) is higher than that in the other three MYSOs by more than one order of magnitude (Taniguchi et al. 2018b). This ratio will be much lower in some HC$_5$N-undetected MYSOs than the HC$_5$N-detected MYSOs. In fact, Green et al. (2014) did not detect HC$_5$N in half of their target MYSOs.

Figure 7 shows the temporal dependence of the HC$_5$N/CH$_3$OH abundance ratio of Models M1–M3. Because the individual abundances of both HC$_5$N and CH$_3$OH can be reproduced only after desorption from the gas, we investigated the ratio of their abundances only in this region. The actual investigated ranges of age are 4.75 × 10^5–2.48 × 10^6 yr, 5.79 × 10^5–1.02 × 10^6 yr, and 1.16 × 10^6–1.3 × 10^6 yr for Models M1, M2, and M3, respectively. The closest calculated values to the observed ratios are ~0.20 at 6 × 10^5 yr (T = 200 K) in Model M1 and ~0.16 at 1.2 × 10^6 yr (T ≈ 115 K) in Model M3. In the case of Model M2, the calculated ratio with the current time resolution changes too rapidly and we could not find the exact value and age when the observed ratio is reproduced. From Figure 7, the observed ratio may be reproduced around 8 × 10^5 yr (T = 200 K) in Model M2. All of these ages correspond closely to the time when HC$_5$N reaches the peak abundances. These results may suggest that desorption of HC$_5$N or its further gas-phase formation have just started in hot regions in G28.28–0.36.

4.3. Effects of Cosmic Ray Ionization Rates on HC$_5$N Abundance

Fontani et al. (2017) suggested that a high cosmic-ray ionization rate of $\zeta \approx 4 \times 10^{-14}$ s$^{-1}$ can reproduce their observational results for cyanopolynyes in OMC-C2 FIR4. The observational results of the c-C$_2$H$_2$ abundance were also reproduced by such a high cosmic-ray ionization rate (Favre et al. 2018). In addition to runs with the common cosmic-ray ionization rate of $\zeta = 1.3 \times 10^{-17}$ s$^{-1}$, we ran our models with high cosmic-ray ionization rates of $\zeta = 3.0 \times 10^{-16}$ s$^{-1}$ and 4.0 × 10^{-14} s$^{-1}$, as Fontani et al. (2017) had done. Such high cosmic-ray ionization rates could be possible in protostellar systems (Padovani et al. 2016). Our results for gas-phase HC$_5$N abundances using these three ionization rates are shown in Figure 8. We used Models M3 and M1 with Slow and Fast warm-up timescales in panels (a) and (b), respectively.

In panel (a), the peak abundances decrease with an increase in the cosmic-ray ionization rate. This is caused by the fact that HC$_5$N is destroyed in the gas phase by reaction with H$^+$ and other ions before it is adsorbed onto dust grains. The H$^+$ ion destroys HC$_5$N most efficiently after 7 × 10^5 yr.

\[
\text{HC}_5\text{N} + \text{H}^+ \rightarrow \text{H} + \text{HC}_5\text{N}^+. \tag{20}
\]
observed abundance in G28.28–0.36 even at peak abundance. However, there is no significant difference in peak abundance among the fast warm-up models with different cosmic-ray ionization rates in panel (b). With the highest cosmic-ray ionization rate, HC$_5$N continues to be formed by Reaction (11) efficiently, while the reaction is less efficient due to the significantly lower abundance of C$_4$H$_2$ in the models with the cosmic-ray ionization rate of $3.0 \times 10^{-16}$ s$^{-1}$ after $\sim 1 \times 10^6$ yr. This highest cosmic-ray ionization model can reproduce the observed abundance in G28.28–0.36 for all times after $4.86 \times 10^5$ yr ($T \geq 170$ K).

The HC$_5$N abundance in the slow warm-up model with cosmic-ray ionization rate of $4.0 \times 10^{-14}$ s$^{-1}$ is significantly lower than in the same cosmic-ray ionization rate model with fast warm-up. The difference between slow and fast warm-up models is caused by the different abundances of H$^+$ and H$_3^+$, which in turn are related to the abundances of H and H$_2$. In the slow warm-up model, the H$_2$ formation rate is slowed down by an exponential factor of the form $\exp\left(-\frac{E_{\text{diff}}}{T}\right)$, where $E_{\text{diff}}$ is known as the diffusion barrier and $T$ is the temperature. The diffusion barrier slows the average motion of the reacting hydrogen atoms. The destruction rate of H$_2$ is larger than its formation rate in such a high cosmic-ray ionization condition. The retarding effect of the diffusion barrier is lessened in the fast warm-up model because of the higher temperatures even at early times. Hence, the H abundance is higher than that of H$_2$ in the slow warm-up model, while the H$_2$ abundance is higher in the fast warm-up model. In the slow warm-up model, the H$^+$ ion is efficiently formed by the ionization of H atoms by cosmic rays. On the other hand, in the fast warm-up model, the H$^+$ ion is formed by the reaction between H$_2$ and cosmic rays, leading to H, H$^+$, and electrons, which is slower than the ionization of H atoms by cosmic rays. Hence, the formation of the H$^+$ ion is more efficient in the slow warm-up model. Cosmic rays also produce H$_2^+$ from H$_2$ ionization. The H$_2^+$ ion subsequently reacts with H$_2$ forming the H$_3^+$ ion in the fast warm-up model, whereas H$_2^+$ reacts with H to form H$_2$ and H$^+$ in the slow warm-up model. Therefore, in the slow warm-up model, the H$^+$ abundance is larger than that of H$_3^+$, while the opposite is true in the fast warm-up model.

The H$^+$ ion contributes to destruction of HC$_5$N to form HC$_5$N$^+$ in the slow warm-up model. The reaction between HC$_5$N$^+$ and electrons cannot produce HC$_5$N. In the fast warm-up model, on the other hand, the reactions with H$_3^+$ and HCO$^+$ destroy HC$_5$N, and both reactions form HC$_5$N$^+$, which reacts with electron and partially goes back to HC$_5$N. Reaction (11) continues to form HC$_5$N in both models and this reaction is particularly important for the slow warm-up model. The C$_4$H$_2$ molecules are formed from large hydrocarbons (e.g., C$_3$H$_4$) and their ions (e.g., C$_4$H$_7^+$) in both models, not bottom-up formation starting from CH$_4$. Therefore, the carbon-chain formation starting from CH$_4$ is no longer an important formation mechanism of cyanopolyynes for the highest cosmic-ray ionization models.

In summary, the lower limit of HC$_5$N observed in the G28.28–0.36 MYSO can be reproduced with temperatures above $\sim 115$ K in all of the models with the typical cosmic-ray ionization rate of $1.3 \times 10^{-17}$ s$^{-1}$. In the case of the Slow warm-up timescale, the models with high cosmic-ray ionization rates cannot reproduce the observed abundance of HC$_5$N in G28.28–0.36. On the other hand, the model with Fast warm-up

\[ \text{HC}_5\text{N} + \text{HCO}^+ \rightarrow \text{CO} + \text{H}_2\text{C}_5\text{N}^+. \]  

(21)
timescale and the highest cosmic-ray ionization rate can maintain the high abundance of HC5N.

4.4. Comparisons among Carbon-chain Species

We found unusual features of the cyanopolyynes during the warm-up period: in particular, they are formed initially in the gas phase, subsequently accumulate in the bulk of the icy mantle, and then desorb into the gas phase, with their gas-phase peak abundances attained when they desorb. The carbon-chain molecule CH$_3$CCH shows a similar feature (Section 4.2).

Figure 9 shows the abundances of CCH (red), CCS (green), and c-C$_3$H$_2$ (blue) during the warm-up period. The species CCH and CCS show abundance peaks just after the temperature rises to 25 K. The CCH molecule is efficiently destroyed by the reaction with atomic oxygen (O) during $1.0 \times 10^5 \leq t \leq 1.07 \times 10^6$ yr, when the temperature rises from $\approx 70$ K to $\approx 80$ K. The subsequent decrease in the gas-phase CCH abundance is caused by its efficient destruction by reaction with H$_2$, which occurs efficiently with the temperature of $\geq 90$ K, at a time of $t \geq 1.1 \times 10^6$ yr (Hassel et al. 2011). Dicarbon sulfide, or CCS, is destroyed by the reaction with atomic oxygen (O). The atomic oxygen desorbs at temperatures above 60 K (He et al. 2015) at a time of $t \geq 1.0 \times 10^6$ yr. Because of these rapid gas-phase reactions, desorption from dust surfaces is not important for the synthesis of gas-phase CCH and CCS.

On the other hand, c-C$_3$H$_2$ shows its gas-phase peak abundance after its direct evaporation from the dust surface at temperatures above 90 K at a time of $t \geq 1.1 \times 10^6$ yr, as is the case for the cyanopolyynes and CH$_3$CCH. The cyclic species c-C$_3$H$_2$ is produced in the gas-phase both in the pre-warm-up period and during the warm-up period starting with the sublimation of CH$_4$. The main formation pathway of c-C$_3$H$_2$ is the dissociative recombination reaction of c - C$_3$H$_3^+$:

$$c - C_3H_3^+ + e^- \rightarrow c - C_3H_2 + H.$$ (22)

Gaseous c-C$_3$H$_2$, formed in the low-temperature portion of the warm-up period, is subsequently adsorbed onto dust grains, from which it desorbs after $\sim 1.0 \times 10^6$ yr at temperatures $T \geq 65$ K. It is efficiently destroyed by the reaction with H$_2$ at temperatures above 120 K ($t \geq 1.2 \times 10^6$ yr). Hence, the efficient destruction of c-C$_3$H$_2$ occurs after it desorbs. All species in Figure 9 decrease in abundance with parallel curves after $1.5 \times 10^6$ yr.

In summary, there are largely two types of carbon-chain species in warm-up regions. One type shows peak abundances just after their desorption from dust grains; these include cyanopolyynes, CH$_3$CCH, and c-C$_3$H$_2$. The other type shows peak abundances just after the temperature rises to 25 K (CCH and CCS). The latter include relatively reactive species, which are easily destroyed in the gas phase. On the other hand, cyanopolyynes are not destroyed by reactions with H$_2$ and O, but react with ions such as H$^+$, H$_3^+$, and HCO$^+$, and so eventually decrease.

Such differences among carbon-chain species seem to explain the observational results in HMPOs (Taniguchi et al. 2018c, 2019) and massive cluster-forming regions (Shimoikura et al. 2018). Taniguchi et al. (2018c) suggested that HC$_3$N is newly formed in the warm and well shielded dense gas around HMPOs, and Taniguchi et al. (2019) reported that the detection rates for the cyanopolyynes, defined by the number of sources where target molecules were detected divided by the number of total observed sources ×100, are higher around HMPOs than in low-mass protostars, but that of CCS is lower. Shimoikura et al. (2018) concluded that HC$_3$N tends to be abundant, whereas CCS detection is rare in massive cluster-forming clumps, where it has probably been already destroyed by reaction with O because the dust temperature should be higher than the sublimation temperature of atomic oxygen. On the other hand, HC$_3$N can still be abundant in such high temperature regions.

4.5. Implication for Chemical Diversity around MYSOs

As already mentioned in Section 1, the different timescales of the starless core phase (Sakai & Yamamoto 2013) and the penetration of the interstellar radiation field (Spezzano et al. 2016) were proposed as possible origins of chemical diversity in low-mass star-forming regions. High-mass stars are usually born in giant molecular clouds (GMCs), and there is a possibility that the formation of HMCs starts long after the clouds were well shielded against the interstellar radiation field unless GMCs have clumpy structures. In the former case, there should be enough time for atomic carbon to convert into CO molecules. In particular, the interstellar radiation field may be important for the outer edge of GMCs but not for the inner regions, as is the well-known case of photon-dominated regions.

Chemical diversity can also be caused by the dependence of abundance on the heating rate. For example, CH$_3$OH shows higher peak abundances in those models with a Fast heating timescale. On the other hand, as discussed above, HC$_3$N tends to be more abundant in the models with the Slow heating timescale because there is enough time for HC$_3$N to accumulate in the bulk of the icy mantle before desorption. This may be one possible origin of the chemical diversity around MYSOs (Taniguchi et al. 2017, 2018b).

The heating timescale of warm-up regions depends not only on stellar masses but also on the relationship between the size of the warming region and the infall velocity (Aikawa et al. 2008) as given by

$$\tau_h \propto \frac{R_{\text{warm}}}{V_{\text{infall}}}.$$ (23)

where $\tau_h$, $R_{\text{warm}}$, and $V_{\text{infall}}$ are the heating timescale, the size of the warm region, and the infall velocity, respectively. If $R_{\text{warm}}$
becomes larger or \( V_{\text{infall}} \) becomes smaller, \( t_h \) will be longer. Such a condition will lead to HC\(_5\)N-rich/CH\(_3\)OH-poor envelopes around MYSOs, which is similar to the case of G28.28−0.36.

The size of warm regions and their infall velocity relate to other physical conditions. For example, the size of warm regions depends upon the luminosity of the central stars, and the density structure (Nomura & Millar 2004), while the infall velocity is related to the density, rotating motion, magnetic field, and radiation pressure (e.g., Sugiyama et al. 2014). Consequently, the heating timescale is also related to the physical conditions in star-forming regions. Observations investigating relationships between the chemical diversity and Equation (23) are necessary to constrain the proposed scenario.

The possibility of UV radiation to cause chemical diversity should be considered in cluster regions. The first born star should affect its environment and the strong UV radiation it emits can destroy CO molecules to form C and/or C\(^+\), which will be precursors of carbon-chain species. In that case, we would expect chemical diversity among sources in the same cluster region. As discussed in Section 4.3, the cosmic-ray ionization rate significantly affects the abundances of cyanopolyynes. Cosmic rays can penetrate deeper dense regions compared to the UV radiation. Hence, the effects of cosmic rays may be essential particularly in the dense cores including hot cores.

The binding energies are affected by significant errors (Table 6 in the Appendix) and they change with ice-mantle surface composition (e.g., Nguyen et al. 2018). More laboratory work should be dedicated to binding energy measurements; meanwhile, detailed comparison between model predictions and observational results toward star-forming regions will help to put constraints on these important parameters.

5. Conclusions

We have investigated cyanopolyne chemistry around MYSOs with warm-up hot-core models using the Nautilus code, and motivated by recent observational results toward MYSOs (Taniguchi et al. 2017, 2018b). The main conclusions of this paper are as follows:

1. Cyanopolyynes are formed via neutral–neutral and ion–neutral reactions in the lukewarm gas (25 < \( T < 100 \) K). The sublimation of CH\(_4\) and C\(_{2n}\)H\(_2\) from dust grains enhances key reactions for the formation of cyanopolyynes. They are simultaneously accumulated on the dust surface and in the bulk of icy mantles in this temperature range. Cyanopolyynes sublimate into the gas phase when the temperature rises above \( \sim 100 \) K and reach their peak abundances in the gas phase.

2. The carbon-chain species CH\(_3\)CCH shows similar characteristics to cyanopolyynes. It is formed from CH\(_4\) sublimated from dust grains and accumulates onto dust grains before the temperature reaches its sublimation temperature of 70 K. After the temperature reaches 70 K, CH\(_3\)CCH desorbs from dust grains and shows its gas-phase peak abundance.

3. Models with a longer warm-up period enable these species to accumulate to a greater extent in the bulk of icy mantles.

4. Our model results can reproduce the lower limits of HC\(_3\)N, CH\(_3\)CCH, and CH\(_3\)OH observed in the G28.28−0.36 MYSO, where HC\(_3\)N is particularly abundant (Taniguchi et al. 2017). Their observed abundances are reproduced best just after their sublimation from dust grains.

5. The species CCH and CCS show their peak abundances just after they are formed in the gas phase triggered by the evaporation of CH\(_4\). The chemistry that produces them is the WCCC chemistry. They are reactive species and destroyed by H\(_2\) or O in the gas phase. On the other hand, cyanopolyynes, CH\(_3\)CCH, and c-C\(_3\)H\(_2\) are relatively stable species and can accumulate in the bulk of icy mantles before destruction in the gas phase. This implies that there are largely two types of carbon-chain species. Such results seem to explain the higher detection rates of cyanopolyynes than that of CCS in HMPOs and cluster-forming regions.

6. HC\(_3\)N-rich and CH\(_3\)OH-poor envelopes around MYSOs may reflect different heating timescales. The heating timescale depends not only on the mass of central stars but also on the relationships between the size of warm regions and their infall velocity, which in turn relate to various physical conditions, including luminosity, density, magnetic field, rotating motion, and radiation pressure.

K.T. would like to thank the University of Virginia for providing the funds for her postdoctoral fellowship in the Virginia Initiative on Cosmic Origins (VICO) research program. E.H. is grateful for support from the National Science Foundation through grant AST-1514844.

Software: Nautilus (Ruaud et al. 2016).

Appendix

Binding Energy

Table 6 summarises binding energies of major species and key species in this paper utilized in our model. These binding energy values and errors are taken from the KIDA database (Wakelam et al. 2017).

| Species | Binding Energy (K) | Species | Binding Energy (K) |
|---------|-------------------|---------|-------------------|
| H       | 650 ± 195         | C\(_2\)H\(_2\) | 2587 ± 776        |
| H\(_2\) | 440 ± 132         | C\(_2\)H\(_2\) | 4187              |
| C       | 4000              | C\(_2\)H\(_2\) | 5787              |
| O       | 1660 ± 60         | HC\(_3\)N | 4580              |
| N       | 800               | HC\(_3\)N | 6180              |
| CO      | 1150              | HC\(_3\)N | 7780              |
| CN      | 1600              | CH\(_3\)OH| 5534              |
| CH\(_4\) | 1300             | CH\(_3\)CCH| 4287              |

Note. These values are applied for species on amorphous water ice surface (Wakelam et al. 2017).
ORCID iDs

Kotomi Taniguchi https://orcid.org/0000-0003-4402-6475
Eric Herbst https://orcid.org/0000-0002-4649-2536
Paola Caselli https://orcid.org/0000-0003-1481-7911
Alec Paulive https://orcid.org/0000-0002-6001-8048
Dominique M. Maffucci https://orcid.org/0000-0002-4483-1733
Masao Saito https://orcid.org/0000-0003-0769-8627

References

Acharyya, K., & Herbst, E. 2017, ApJ, 850, 105
Aikawa, Y., Wakelam, V., Garrod, R. T., & Herbst, E. 2008, ApJ, 674, 984
Balucani, N., Ceccarelli, C., & Taquet, V. 2015, MNRAS, 449, L16
Belloche, A., Müller, H. S. P., Menten, K. M., Schilke, P., & Comito, C. 2013, A&A, 559, A47
Benson, P. J., Caselli, P., & Myers, P. C. 1998, ApJ, 506, 743
Bergantini, A., Góbi, S., Abplanalp, M. J., & Kaiser, R. I. 2018, ApJ, 852, 70
Beuther, H., Schilke, P., Menten, K. M., et al. 2002, ApJ, 566, 945
Bonfand, M., Belloche, A., Menten, K. M., Garrod, R. T., & Müller, H. S. P. 2017, A&A, 604, A60
Burkhardt, A. M., Herbst, E., Kalenskii, S. V., et al. 2018, MNRAS, 474, 5068
Caselli, P., & Ceccarelli, C. 2012, ARA&A, 20, 56
Esplugues, G. B., Cernicharo, J., Viti, S., et al. 2013, A&A, 559, A51
Favre, C., Ceccarelli, C., López-Sepulcre, A., et al. 2018, ApJ, 859, 136
Fontani, F., Ceccarelli, C., Favre, C., et al. 2017, A&A, 605, A57
Garrod, R. T. 2013, ApJ, 765, 60
Garrod, R. T., & Herbst, E. 2006, A&A, 457, 927
Green, C.-E., Green, J. A., Burton, M. G., et al. 2014, MNRAS, 443, 2252
Hassel, G. E., Harada, N., & Herbst, E. 2011, ApJ, 743, 182
Hassel, G. E., Herbst, E., & Garrod, R. T. 2008, ApJ, 681, 1385
Herbst, E., & Millar, T. J. 2008, in Low Temperatures and Cold Molecules, ed. I. W. M. Smith (Singapore: World Scientific), 1
Herbst, E., & van Dishoeck, E. F. 2009, ARA&A, 47, 427
Hirota, T., Ohishi, M., & Yamamoto, S. 2009, ApJ, 699, 855
Hudson, R. L., & Moore, M. H. 2018, ApJ, 857, 89
Jaber Al-Edhari, A., Ceccarelli, C., Kahane, C., et al. 2017, A&A, 597, A40
Jørgensen, J. K., Schöier, F. L., & van Dishoeck, E. F. 2002, A&A, 389, 908
Lee, H.-H., Herbst, E., Pineau des Forets, G., Roueff, E., & Le Bourlot, J. 1996, A&A, 311, 690
Li, X., Heays, A. N., Visser, R., et al. 2013, A&A, 555, A14
McGuire, B. A., Burkhardt, A. M., Kalenskii, S., et al. 2018, Sci, 359, 202
Nguyen, T., Baouche, S., Congiu, E., et al. 2018, A&A, 619, A111
Nomura, H., & Millar, T. J. 2004, A&A, 414, 409
Padovani, M., Marcowith, A., Hennebelle, P., & Ferrière, K. 2016, A&A, 590, A8
Rebossin, L., Wakelam, V., Guilloteau, S., & Hersant, F. 2014, MNRAS, 440, 3557
Ruda, M., Wakelam, V., & Hersant, F. 2016, MNRAS, 459, 3756
Sakai, N., Sakai, T., Hirota, T., Burton, M., & Yamamoto, S. 2009, ApJ, 697, 769
Sakai, N., Sakai, T., Hirota, T., & Yamamoto, S. 2008, ApJ, 672, 371
Sakai, N., & Yamamoto, S. 2013, ChRv, 113, 8981
Shimoikura, T., Dobashi, K., Nakamura, F., Matsumoto, T., & Hirota, T. 2018, ApJ, 855, 45
Shingledecker, C. N., & Herbst, E. 2018, PCCP, 20, 5359
Skouteris, D., Balucani, N., Ceccarelli, C., et al. 2018, ApJ, 854, 135
Spezzano, S., Bizzocchi, L., Caselli, P., Harju, J., & Brünken, S. 2016, A&A, 592, L11
Sugiyama, K., Fujisawa, K., Doi, A., et al. 2014, A&A, 562, A82
Suzuki, H., Yamamoto, S., Ohashi, M., et al. 1992, ApJ, 392, 551
Taniguchi, K., Miyamoto, Y., Saito, M., et al. 2018a, A&A, 606, 32
Taniguchi, K., Ozeki, H., Saito, M., et al. 2016a, ApJ, 817, 147
Taniguchi, K., & Saito, M. 2017, PASJ, 69, L7
Taniguchi, K., Saito, M., Hirota, T., et al. 2017, ApJ, 844, 68
Taniguchi, K., Saito, M., Majumdar, L., et al. 2018b, ApJ, 866, 150
Taniguchi, K., Saito, M., & Ozeki, H. 2016b, ApJ, 830, 106
Taniguchi, K., Saito, M., Sridharan, T. K., & Minamidani, T. 2018c, ApJ, 854, 133
Taniguchi, K., Saito, M., Sridharan, T. K., & Minamidani, T. 2019, ApJ, 881, 133
van Dishoeck, E. F. 2018, in IAU Symp. 332, Astrochemistry VII: Through the Cosmos from Galaxies to Planets (Cambridge: Cambridge Univ. Press), 3
Visser, R., van Dishoeck, E. F., & Black, J. H. 2009, A&A, 503, 323
Viti, S., Collings, M. P., Dever, J. W., McCoustra, M. R. S., & Williams, D. A. 2004, MNRAS, 354, 1141
Wakelam, V., Loisien, J.-C., Mereau, R., & Ruda, M. 2017, MolAs, 6, 22