Chemical Variations Across the TMC-1 Boundary: Molecular Tracers from the Translucent Phase to the Dense Phase

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Abstract

We investigated the chemical evolutions of gas-phase and grain-surface species across the Taurus molecular cloud-1 (TMC-1) filament from the translucent phase to the dense phase. By comparing observations with modeling results from an up-to-date chemical network, we examined the conversion processes for the carbon-, oxygen-, nitrogen-, and sulfur-bearing species, i.e., from their initial atomic form to their main molecular reservoir form both in the gas phase and on the grain surface. The conversion processes were found to depend on the species and AV. The effect of initial carbon-to-oxygen elemental abundances ratio (C/O) by varying O on the chemistry was explored, and an initial carbon elemental abundance of 2.5 × 10^{-4} and a C/O ratio of 0.5 could best reproduce the abundances of most observed molecules at TMC-1 CP, where more than 90 molecules have been identified. Based on the TMC-1 condition, we predicted a varied grain ice composition during the evolutions of molecular clouds, with H2O ice as the dominant ice composition at AV > 4 mag, CO2 ice as the dominant ice composition at AV < 4 mag, while CO ice severely decreased at AV around 4–5 mag.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Chemical abundances (224); Interstellar medium (847); Interstellar molecules (849)

1. Introduction

Understanding the chemical evolution during the transformation of atomic gas to molecular gas of the clouds is crucial to construct a complete picture of the evolutions of the interstellar medium (ISM). In the transition phase of molecular clouds, such as from the diffuse phase to the translucent phase and then to the dense phase, physical changes of the environments affect the local chemical states. Molecules and their associated chemistry, such as hydrocarbon chemistry, sulfur-containing molecular chemistry, and complex organic molecular chemistry, are imprints of the evolutions of ISM. The choice of suitable tracers that represent the chemistry could reflect the changes of physical processes as well, thus the evolution of star formation (Aikawa et al. 2001).

One process in such a transitional phase is the transformation of atomic hydrogen to molecular hydrogen on the grain surface at low temperatures (Cuppen et al. 2006). Another set of widely recognized process is the transformations between C+, C, and CO during the transition from the diffuse phase to the dense phase of a cloud (Lee et al. 1996). The transformations of species from atomic to molecular form, or from simple to complex form indicate that the chemical complexity is increasing with the evolution of the clouds. Thus, it is worth exploring other kinds of molecules, such as sulfur-bearing molecules and grain-surface species, as tracers in these transitional phases. Moreover, the boundaries defined by different tracers may be characterized by different physical conditions, such as the density or temperature (Goldsmith et al. 2010). Thus, the study of the chemistry of different molecules could benefit our understanding of the physical environments.

The elemental sulfur abundance is severely depleted in dark clouds while maintaining its atomic form in diffuse clouds (Vidal et al. 2017; Laas & Caselli 2019). Thus, there should be a transformation for sulfur-bearing species if we analogize the sulfur chemistry with the carbon chemistry. As stated above, dust grains are important for the formation of H2. Other species could also stick onto the surface of grains, diffuse among the sites and recombine to form new species. Water ice is generally observed on the line-of-sight dense clouds toward background stars. At the diffuse ISM condition, water ice is expected by the laboratory experiments (Potapov et al. 2021). However, there was no strong evidence for the existence of solid-state water in the diffuse–dense transition (Poteet et al. 2015). The presence of water ice is important for the depletion of elemental oxygen in the gas of diffuse ISM, which could be explained if the missing oxygen is in the oxygen-bearing solid form in the grain ice mantles (Poteet et al. 2015). On the other hand, the detection of larger complex molecules, such as CH3OH in the diffuse and translucent clouds (Thiel et al. 2017; Liszt et al. 2018) could also be explained by the grain-surface origin. The chemical composition of grain ice mantles in the diffuse–dense transition is poorly constrained because of the observational difficulty in the identification of interstellar ice mixture. Esplugues et al. (2019) studied the ice chemistry in the photodissociation regions (PDRs) where high UV radiation is present, which results in poor ice compositions (i.e., less than
one monolayer when $A_V < 2$ mag). With respect to the PDRs, the UV radiation in the outer extended regions of the dark clouds is much lower, so that a relatively rich ice composition could be developed in that region. Thus, the comparison of the ice composition between the outer and inner regions of the dark clouds could be more meaningful compared with the PDRs.

The Taurus molecular cloud (TMC) has been chosen as the target by Goldsmith et al. (2010), Xu et al. (2016), and Xu & Li (2016) to study the boundary conditions indicated by H$_2$ emission, OH, and CH physicochemical properties, respectively. Taurus molecular cloud-1 (TMC-1) is one of a nearest clouds with a distance of $\sim 140$ pc (Elias 1978). It is in a place where the low-mass star formation process is ongoing and is currently close to gravitational equilibrium (Fehér et al. 2016). It is also in an environment that is less affected by the external radiation field (Xu et al. 2016) compared with the PDRs, making it an ideal source for the study of chemical evolutions.

Observationally, many species have been detected in the diffuse and translucent phases, indicating that chemical complexity has been developed in these regions (Snow & McCall 2006; Sakai et al. 2012; Liszt et al. 2018). With relatively low density and low extinction, many small hydrocarbons and ions survived (Lucas & Liszt 2000; Liszt et al. 2018; Thiel et al. 2019). With the accretion of the gas, the molecular species diversity also increases. Examples are the detection of cyanopolyne species (Suzuki et al. 1992), methanol, and even more complex organic molecules (COMs; Soma et al. 2015, 2018) in the dense part of TMC-1. More recently, more than two dozen of molecules have been detected in TMC-1, including long carbon chain molecules (Xue et al. 2020; Cabezas et al. 2021a; Cernicharo et al. 2021b; Loomis et al. 2021; Marcelino et al. 2021; Shingledecker et al. 2021), circular and aromatic molecules (Burkhardt et al. 2021; Cernicharo et al. 2021a; McGuire et al. 2021), unsaturated hydrocarbons (Agúndez et al. 2021a; Cabezas et al. 2021b; Cernicharo et al. 2021d), oxygen-bearing COMs (Cernicharo et al. 2020a, 2021e; Agúndez et al. 2021b), sulfur-bearing molecules (Cernicharo et al. 2021e, 2021f), and nitrile anions (Cernicharo et al. 2020b). A systematic check of the chemistry based on this large number of observed molecules could give a new insight into the constraints of the chemical reaction network.

Many observational and theoretical studies have focused either on the chemistry in the diffuse or translucent part (Lucas & Liszt 2000; Liszt et al. 2018; Thiel et al. 2019) with extinctions less than $\sim 5$ mag or on the dense part of TMC-1 CP (the cyanopolyynes emission peak) or TMC-1 NH$_3$ (the ammonia emission peak) and TMC-1 C (the dust continuum peak). As shown in Figure 1 of Fuente et al. (2019), starting from the three emission peaks, there are six cutting points extending horizontally to the edge of the molecular cloud. They represent the transitional regions from the inner dense phase to the outer translucent phase. The physical conditions of the model are derived from Fuente et al. (2019) and which for each point the dust temperature, gas temperature, H$_2$ column density, and volume density were derived. The dust temperature is derived from the Herschel Gould Belt Survey, and the gas temperature and $n$(H$_2$) are derived by fitting the molecular lines of CS and its isotopologues. The extinction is derived by $N$(H$_2$) = $A_V \times 10^{21}$. The total hydrogen nuclei density $n_H$ equals $n$(H) + 2$n$(H$_2$). Here we assume the majority of matter is occupied by H$_2$; thus $n_H \approx 2n$(H$_2$). We list these physical parameters in Table 1.

### 2. Physicochemical Models of the TMC-1 Boundary

#### 2.1. Physical Parameters Description

Along and near the TMC-1 filament, there are three observational emission peaks, namely, TMC-1 CP (the cyanopolyynes emission peak), TMC-1 NH$_3$ (the ammonia emission peak), and TMC-1 C (the dust continuum peak). As shown in Figure 1 of Fuente et al. (2019), starting from the three emission peaks, there are six cutting points extending horizontally to the edge of the molecular cloud. They represent the transitional regions from the inner dense phase to the outer translucent phase. The physical conditions of the model are derived from Fuente et al. (2019) in which for each point the dust temperature, gas temperature, H$_2$ column density, and volume density were derived. The dust temperature is derived from the Herschel Gould Belt Survey, and the gas temperature and $n$(H$_2$) are derived by fitting the molecular lines of CS and its isotopologues. The extinction is derived by $N$(H$_2$) = $A_V \times 10^{21}$. The total hydrogen nuclei density $n_H$ equals $n$(H) + 2$n$(H$_2$). Here we assume the majority of matter is occupied by H$_2$; thus $n_H \approx 2n$(H$_2$). We list these physical parameters in Table 1.

#### 2.2. Chemical Model Description

We use the two-phase (gas phase and grain surface) model of NAUTILUS (Ruaud et al. 2016) to perform the astrochemical simulations. The full gas–grain reaction network is the same as used in Vidal et al. (2017), which is considered the up-to-date sulfur chemistry to solve the elemental sulfur depletion problem, and has been tested at the TMC-1 CP. This network is based on kida.uva.2014 (Wakelam et al. 2015) and Garrod & Herbst (2006). We also modified the network with additional reactions related to C$_2$H and C$_3$H$_2$ isomers from Loison et al. (2017), namely, linear and cyclic configuration, which are widely detected in the interstellar medium including in the diffuse and translucent environments (Turner 2000; Gerin et al. 2011).

Basically, kida.uva.2014 is the gas-phase network, which includes various types of reactions, such as ion–neutral and neutral–neutral reactions, cosmic-ray and UV-photon dissociations. In addition to the gas-phase chemical reactions, there are also grain-surface reactions, and interchange processes between gas-phase and grain-surface species. The gas-phase species can be adsorbed to and diffuse on the grain surface and react with other surface species. In addition to including the thermal desorption and cosmic-ray desorption of grain-surface species,
the network also includes chemical desorption, which is the desorption by exothermicity of surface reactions (Garrod et al. 2007) with an efficiency of 0.01. The ratio of diffuse to emission energy of a grain-surface species is set as the default value of 0.4 (Garrod & Herbst 2006; Chang & Herbst 2012). As for the strength of the interstellar radiation field, the cosmic-ray ionization rate is set as 5 times the standard value of $1.3 \times 10^{-17}$ s$^{-1}$, and the UV factor is set as 3.8 in Habing units. These two values are consistent with the PDR model results (Fuente et al. 2019) where different values of cosmic-ray ionization and the UV factor are used to fit the gas ionization fraction and the relation between dust temperature and $A_V$, respectively. We do not distinguish the difference between the grain surface and grain ice mantle species. As for other parameters used in the model, the gas-to-dust mass ratio is 100, and we assume a spherical silicate dust grain, with a commonly used radius of 0.1 $\mu$m and a density of 3 g cm$^{-3}$. We also assume that the number density of grain-surface sites is $1.5 \times 10^{15}$ cm$^{-2}$.

Due to the low extinction in the boundary of the TMC-1 filament, as shown in Table 1, the shielding for H$_2$ and CO should be important. NAUTILUS includes the self-shielding of H$_2$ (Lee et al. 1996), CO self-shielding and cross shielding by H$_2$ and dust (Visser et al. 2009), and the shielding of N$_2$ by H$_2$ and N$_2$ (Li et al. 2013).

The initial elemental abundances are chosen from Semenov et al. (2010) with the exception of C$^+$, O and, S$^+$ because of the importance of these elements on the chemistry. Agúndez & Wakelam (2013) have shown that a carbon-poor, oxygen-rich condition (C/O $= 0.55$) could reproduce over 60% modeled species within 1 order of magnitude compared with observed molecules at TMC-1 CP, while for the cyanopolyynes species (HC$_3$N, $n = 3, 5, 7, 9$), they are more favored in the opposite condition (with C/O $= 1.2$), as shown by Maffucci et al. (2018). On the other hand, the sulfur element depletion is an unsolved problem (Jenkins 2009; Vidal et al. 2017; Vastel et al. 2018). It is known that sulfur remains in its ionized atomic form in diffuse and translucent interstellar media (Jenkins 2009; Laas & Caselli 2019) at an abundance of its cosmic value, while it is severely depleted in the gas phase of the dense clouds or cores in almost 3 orders of magnitude (Agúndez & Wakelam 2013; Laas & Caselli 2019). This problem is raised partially because of the insufficient sulfur chemical reactions in the network, so that observational values can only be reproduced when the depleted initial elemental sulfur abundance in dense clouds is chosen. With an update of the sulfur reactions, Vidal et al. (2017) showed that an undepleted elemental sulfur abundance, which corresponds to its cosmic value, could also fit the observations in the dense clouds condition. Thus, a universal value of the initial sulfur elemental abundance is used throughout the simulations range from different transitional phases of the clouds. Table 2 shows the initial elemental abundances.

### 3. Results and Analysis

We show the results in this section. We first constrain the initial carbon and oxygen elemental abundances for the chemical models by comparing the observational molecular abundances at the TMC-1 CP with our modeled abundances. The TMC-1 CP is one of the famous targets for many observations. There are over 90 molecules have been detected at this location. See Ohishi et al. (1992), Kaifu et al. (2004), Adande et al. (2010), Agúndez & Wakelam (2013), Gratier et al. (2016), McGuire et al. (2017), and recent observational references in the previous section. We divide these molecules into four groups according to their elemental characteristics and the role they played in the reaction network. The S group represents all species that include the sulfur element. The N group represents nitrogen-containing species excluding S group species. The O group represents oxygen-containing species.

| Element | Abundance |
|---------|-----------|
| H$_2$   | 0.5       |
| He      | 9.00(−2)  |
| C$^{13}$ | 1.2(−4), 1.8(−4), 2.5(−4) |
| O$^+$   | varied    |
| N       | 7.60(−5)  |
| S$^{16}$ | 1.50(−5)  |
| Si$^+$  | 8.00(−9)  |
| Mg$^+$  | 7.00(−9)  |
| Fe$^+$  | 3.00(−9)  |
| Na$^+$  | 2.00(−9)  |
| Cl$^+$  | 1.00(−9)  |
| P$^+$   | 2.00(−10) |

Notes. a(−b) represents $a \times 10^{-b}$. All other values are cited from Semenov et al. (2010).

a Three different values are tested; see Section 3.1. The low, intermediate, and high values are taken from Semenov et al. (2010), Agúndez & Wakelam (2013), and Przybilla et al. (2008), respectively.

b Calculated with varied C/O ratio range from 0.4 to 1.4.

c Cited from Vidal et al. (2017).
excluding S and N group species. Finally, the C group represents the remaining species. These are mainly hydrocarbons that only include the hydrogen and carbon element. This group also includes the atomic carbon and diatomic carbon.

3.1. Chemical Variations at the TMC-1 CP Emission Peak

As introduced previously, the initial carbon-to-oxygen elemental abundances ratio (C/O) is important for chemistry in the ISM. In this section, we first explore the variations in this ratio with the chemistry. We keep the initial carbon elemental abundance fixed and vary the C/O to derive the initial oxygen elemental abundance. To explore the variations in the initial carbon abundance, we use three different values corresponding to low, intermediate, and high abundance, which are $1.2 \times 10^{-4}$ (Semenov et al. 2010), $1.8 \times 10^{-4}$ (Agúndez & Wakelam 2013), and $2.5 \times 10^{-4}$ (Przybilla et al. 2008), respectively, while the C/O ratio is varied from 0.4 (Lee et al. 1996) to 1.4 (Agúndez & Wakelam 2013) with a step size of 0.1. In the following, we show our best-fit model results, followed by a discussion on the chemistry due to the variations in the C/O ratio.

3.1.1. Best-fit Model

By comparing the observational abundances of the molecules with the calculations from the models, we could determine the best-fit model and the chemical evolutionary timescale of the molecular cloud. We use Equation (1), which is known as the distance of disagreement (Vidal et al. 2017), to calculate the mean logarithmic difference for all detected molecules at every time step

$$D(t) = \frac{\sum_i |\log(X_{\text{mod},i}(t)) - \log(X_{\text{obs},i})|}{N_{\text{obs}}}$$

where $X_{\text{mod},i}(t)$ and $X_{\text{obs},i}$ are the modeling abundance for species $i$ at time $t$ and the observed abundance, respectively, and $N_{\text{obs}}$ is the total number of the observed species.

Figure 1 shows the calculated results for the initial carbon abundance of $2.5 \times 10^{-4}$ and a C/O ratio of 0.5. It can be seen that the best-fit time is located at $\sim 5.3 \times 10^5$ yr. This best-fit time is in good agreement within the range of $4.2 \pm 2.4 \times 10^5$ yr estimated from the CO depletion timescale toward 13 cores in Taurus (Pineda et al. 2010). Moreover, in order to show the diversity of the abundance between the observational value and modeling value of each species, we plot in Figure 2 the logarithmic abundance ratio difference for each observed species. In the figure, the left end point and right end point for each molecule are the minimum and maximum values in the time range of $10^4$ to $10^7$ yr, respectively. The red cross mark corresponds to the time at best agreement, i.e., $5.3 \times 10^5$ yr. The vertical gray area between $-1$ and $+1$ represents 1 order of magnitude lower and higher, respectively, of the observed values.

In Figure 2, there are 66 out of 93 species, which is 71%, whose logarithmic abundance is within the range of $-1$ to $+1$ of observation at the best-fit time. This percentage is similar to the results of earlier studies with a total observed species of $\sim 60$ (Agúndez & Wakelam 2013; Wakelam et al. 2015). Specifically, for the 23 O group molecules, C$_3$O and CH$_3$O are about 2 orders of magnitude overproduced, while large COMs (CH$_3$CHO, HCOOCH$_3$, and CH$_3$(OCH$_3$)$_2$) are underproduced. For the 22 C group molecules, there are 8 species out of the range from $-1$ to $+1$. Most of these out-of-range species are C$_n$H$_{2n+1}$ and C$_n$H$_2$ with $n = 4, 6, 8$. Note that all of the small hydrocarbons with fewer than three carbon elements are much closer to the observations than large hydrocarbons. This trend is also seen in other models, which may indicate the inefficient destruction pathways for the larger hydrocarbons when they grow complex. Nitrogen-bearing molecules in the N group are the most detected species in the TMC-1 CP. Among them, there are 5 out of 28 that are outside the range from $-1$ to $+1$. These are CN, C$_2$N, H$_2$CN, NH$_2$CHO, and HCN, which are arranged from large to small disagreement with respect to their corresponding observed values. Compared with the sequential arrangement for the overproduced small hydrocarbons and large hydrocarbons, there is no such clear arrangement for these nitrogen-bearing molecules.

Finally, about a half of S group species (9 out of 20) are outside the range of 1 order of magnitude of their observational values at the best-fit time. Among them, CS$^+$ is the most underproduced species; the predicted peak fractional abundance with respect to H is $2.2 \times 10^{-11}$ at $\sim 250$ yr and severely decreased after that, while the observed abundance of CS$^+$ is $1.5 \times 10^{-10}$. Compared with CS$^+$, CS is overproduced by 2 orders of magnitude at its best-fit time. The predicted peak abundance of CS is $1.9 \times 10^{-6}$ at $\sim 3.9 \times 10^2$ yr and also decreases after that, while the observed abundance for CS is $1.5 \times 10^{-9}$. In the chemical reaction network, CS is mainly produced by HCS$^+$, and destructed by H$^+$ and H$_3^+$. On the other hand, CS$^+$ is mainly produced by reaction of CH with S, and destructed by electron and H$_2$. Most calculated abundances of the sulfur-bearing species are larger than their observed values. The discussion of these discrepancies will be presented later.

3.1.2. Variation in the C/O Ratio with the Chemistry

We noticed that the predicted abundances of S group species are closer to their observed values when the C/O ratio increases. While the trend for other group species is the
The variation in C/O with the chemistry as expressed by the numbers of the disagreement species for the four groups can be seen in Figure 3, which corresponds to the model with an initial carbon abundance of $2.5 \times 10^{-4}$. The trends for the four groups are also presented for the low and intermediate initial carbon abundance models. The disagreed species are counted when the logarithmic abundance ratio differences between models and observations are out of the range of $-1$ to $+1$ (see Figure 2). Note that the counts are calculated for each model at their own best-fit time.

From Figure 3 it can be seen that the C and O group species favor a C/O ratio of 0.5, and with the increase in the C/O ratio, the disagreement rises greatly. As opposed to the C and O groups, the S group species favor a C/O ratio larger than 1.2, while the overall N group species favor a low C/O ratio similar to the C and O groups. However, the favored low C/O ratio for the overall N group species seems to be in contradiction with the result of Maffucci et al. (2018), which shows that a C/O ratio of 1.2 can better reproduce cyanopolyynes. We plot the mean logarithmic abundance difference for cyanopolyynes in Figure 4 using Equation (1) with $N_{\text{obs}}$ only including HC$_n$N$_n$ where $n = 3, 5, 7, 9$ at the time determined from the total observed species, i.e., the same evolutionary time used in the Figure 3. It can be seen that the minimum value is located at C/O = 1.0, which is close to 1.2, while our best-fit model of C/O = 0.5 is in another minimum location. Generally, as concluded by Maffucci et al. (2018), the increase in C/O enhances the production of cyanopolyynes.

Chemically speaking, at the carbon-poor, oxygen-rich condition (C/O < 1), most of carbon is locked with oxygen.
either in the gas phase or on the grain surface mainly in the form of CO, CO$_2$, and H$_2$CO. While at the carbon-rich, oxygen-poor condition (C/O > 1), part of the carbon-bearing molecules are hydrogenated; thus both in the gas phase and on the grain surface, C$_n$H$_m$ and HC$_n$N are overproduced, where $n$ ranges from 3 to 9, and $m = 2, 3, 4$. The initial nitrogen is in the neutral atomic form and less abundant than carbon. It first reacts with hydrocarbons to form nitriles. Most of species in the N group are nitrile-containing molecules; thus the chemistry of N group species is also affected by the variation of C/O ratio and shows similar trend as with the C and O group species. However, for the subset of HC$_n$N with $n = 3, 5, 7, 9$ in the N group, their abundances could be increased by the overproduced large hydrocarbons when C/O > 1, thus show a better fit with the observations than that at the conditions of C/O < 1. The effect of the variation of C/O on the chemistry of sulfur-containing species in the S group is more complex as the elemental compositions of S group species are largely different from each other, which indicates that the reactions related to S group species are well connected with other group species. From Figure 3 it can be seen that the difference between the maximum and minimum counts for the S group species is only 2, which seems not significant when compared with that of other groups. There are three species, H$_2$CS, H$_2$S, and SO, whose abundances approach their observed values as C/O increased. Instead, the abundance of C$_8$S move away from its observed value. For H$_2$CS and H$_2$S, they share similar production pathways when the C/O ratio changes. However, their destruction involves C$^+$ or C so that they overproduced when C/O < 1. As for SO, it is produced by the reaction between S and OH, which could be affected by the C/O ratio. Generally, at C/O < 1, most S group species are slightly overproduced; on the other hand, with the increase C/O ratio, the abundances of these species tend to approach their observational values at the best-fit time.

3.2. Chemical Variations Along the Transitional Regions

In the above section, by comparison between the model results and the observations in TMC-1 CP, we determined the best initial elemental abundances for carbon and oxygen and the best-fit time. In the following subsections, we show the results of the chemical variations under the predictions at the best-fit time for the transitional regions where $A_V$ ranges from 1 to 20 mag.

3.2.1. H, H$_2$, and Ionization Fraction

As the dominated material, hydrogen is the most abundant element in the ISM both in its atomic form and in its molecular form. In the initial condition of the models, we assume all hydrogen exists in its molecular form. Under this condition, all other species evolved with time. We determine the best-fit time (i.e., $5.3 \times 10^5$ yr) for TMC-1 CP by fitting the abundances of all detected species with their predicted values. At this time, it can be seen from Figure 5 that the corresponding atomic hydrogen abundance at $A_V < 10$ mag is $\sim 10^{-3}$. The mean abundance of atomic hydrogen is $10^{-2.8}$ in TMC and other molecular cloud regions determined by H I Narrow Self Absorption (HINSA; Li & Goldsmith 2003; Krö & Goldsmith 2010). This consistency between predicted and observed H I abundance suggests that the above assumption is reasonable. If all hydrogen exists in its atomic form at the initial stage, the conversion timescale for hydrogen to its molecular form could be longer.

The ionization fraction, or the electron abundance ($x(e^-)$), is a basic physical characteristic of the ISM that has a wide influence on the star formation from the driving of the ion–neutral chemistry to the dynamics between the gas and magnetic field. Goicoechea et al. (2009) estimated the gradients of the ionization fraction in the Horsehead PDR regions from the outer edge to the shielded cores where the value changes from $10^{-4}$ to $10^{-2}$, respectively. Unlike the strong UV field in the Horsehead PDR regions (35 in Habing units; Goicoechea et al. 2009), the UV field in the TMC-1 regions is relatively weak (3.8 in Habing units). There also has a similar ionization fraction gradient (see the right panel in Figure 5). At the edge of TMC-1, the value of $x(e^-)$ is $\sim 10^{-5}$, which is contributed from the ionization of atomic carbon and sulfur and cosmic-ray-induced ionization of H$_2$. In the denser part of TMC-1, the ionization fraction is mainly controlled by the cosmic-ray-induced ionization of H$_2$ because UV photons cannot penetrate into the clouds.

3.2.2. Carbon, Oxygen, and their Carriers

Except for the conversion of atomic hydrogen to molecular hydrogen in the transitional regions, the species of C$^+$, C, and CO are also widely recognized as the evolutionary tracers of these regions. Figure 6 shows the calculated abundances of these three species as a function of $A_V$. It can be seen that the abundance of C$^+$ gradually decreases from the outer low-extinction regions to the inner high-extinction regions. Meanwhile, C$^+$ is partially converted to C and CO, and the abundance of C peaks around $\sim 4$ mag. The conversion of C$^+$ to CO is efficient because of less strength of the UV field in these regions and the shielding from H$_2$ and CO itself. With the continuing increase in $A_V$, eventually most of carbon is locked in the form of CO. Meanwhile, at high $A_V$ and density, gas–grain chemistry plays an important role, and gas-phase CO begins to adsorb onto the grain surface. Thus, we see a depletion of CO after $A_V > 10$ mag. The rate of depletion depends on the gas density; the higher the gas density, the greater the CO depletion rate. In the horizontal extensions of TMC-1 CP, it can be seen that at the location of offset 3 from
the emission peak, CO is severely depleted, and this position represents the highest density. The effect of the gas density also has an influence on the other gas-phase species, as can be seen in the following. Molecules that can be easily synthesized in the gas phase adsorb more quickly onto the grains when the gas density is high, while for gas species with a low synthesis rate, such as some large molecules, the abundances trend to increase under high-density conditions. In comparison, the densities for the horizontal extensions of TMC-1 C and TMC-1 NH$_3$ generally decrease from the inner to the outer region. It should be noted that our results are presented under the same evolutionary times. Some studies have noticed the possible different evolutionary stages for the TMC-1 C and TMC-1 CP emission peaks (Choi et al. 2017; Navarro-Almaida et al. 2021).

Figure 5. Abundances of H I, H$_2$, and e$^-$ as a function of $A_V$. In the left panel, H I is shown by empty markers, while H$_2$ is shown by filled markers. Hereafter, we use the three emission peaks to represent the three horizontal lines that cross the TMC-1 filament boundary.

Figure 6. Abundances of C$^+$, C, and CO as a function of $A_V$. 

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The state of the chemistry could be affected by the different physical conditions and different evolutionary stages of the clouds. However, it is difficult to decouple the effects of these two factors on the chemistry as the different evolutionary stages may have implied the different physical conditions, and it is the focus of our next paper to explore this problem.

The main carriers of oxygen are the atomic oxygen (O I) and CO in the gas phase at $A_V < 10$ mag. It can be seen in Figure 6 that the abundance of atomic oxygen is slightly higher than that of CO before its depletion. Recently, Goldsmith et al. (2021) explored the O I emission and absorption in the W3 high-mass star formation regions. They found that O I is dominated by the foreground absorption of low-excitation atomic oxygen, and its abundance could be comparable to, or greater than that of CO. The highest fractional abundance of O I with respect to H is $6 \times 10^{-5}$ under an initial oxygen abundance of 2.3 $\times 10^{-4}$ in Goldsmith et al. (2021). In our results, the best-fit model uses an initial oxygen abundance of 5.0 $\times 10^{-4}$, and the abundance of O I could be maintained at a level of $\sim 2.0 \times 10^{-4}$ when $A_V < 10$ mag. Thus, the atomic oxygen along with C and C$^+$ could be used as chemical tracers to evaluate the physical properties of the translucent ISM.

Xu et al. (2016) and Xu & Li (2016) also showed that the primary hydrides CH and OH could be used as gas tracers across the TMC boundary. They derived a fractional abundance (with respect to H$_2$) of $\sim 2 \times 10^{-8}$ and $\sim 2 \times 10^{-7}$ for CH and OH at $A_V = 2$ mag, respectively. Compared with our modeling results, our predictions for the abundances of CH and OH are underproduced by a factor of 5 and 30, respectively. Xu et al. (2016) interpreted the reason for the large discrepancy between the modeled and observational OH abundance as the shock, which is originated by the compression of the gas in the cloud's edges. However, the above estimation is under the assumption that all hydrogen is in the form of H$_2$, i.e., the abundance of H$_2$ with respect to the total nuclei is 0.5. If we assume that a fraction of hydrogen is in the atomic form, which is reasonable under the cold neutral medium condition, then the above discrepancy between our predictions and the observations for the abundances of CH and OH could be replaced by a factor of 25 and 5, respectively, when a value of 0.3 for the abundance of H$_2$ with respect to the total nuclei is used. It can be seen that the fraction of atomic hydrogen could be important for the primary gas contents and their chemistry. Therefore, to better understand the chemistry of CH and OH, direct measurement of primary gas contents, such as using the HINSA to determine the properties of clouds (Zuo et al. 2018), could be helpful.

### 3.2.3. $S^+$, $S$, and Main Sulfur-containing Carriers

The cosmic value of the sulfur elemental abundance is used so that we could study the sulfur chemistry across a wide range of $A_V$. We demonstrate in Figure 7 the calculated most abundant gas-phase and surface S-bearing molecules. Similar to the trends of C$^+$ and C as a function of $A_V$, S$^+$ (shown in empty markers) remains in its ionic form when $A_V < 3$ mag and is converted to its neutral atomic form (shown in filled markers) at higher $A_V$. When $A_V > 10$ mag, sulfur is mostly adsorbed onto the grains and hydrogenated to JHS and JH$_2$S subsequently (hereafter, “/’” stands for grain-surface species), as shown in the upper panels of Figure 7. For example, at the TMC-1 CP, which corresponds to an $A_V$ of 18.2 mag, 59% of the total sulfur abundance is in the form of JHS and JH$_2$S, and 20% is occupied by other grain-surface species, such as JHSCN, JHSO, JOCS, and JNS, whereas 15% by the gas-phase neutral atomic sulfur, and the remaining small amount is occupied by other S-bearing species. Gas-phase S-bearing species are mainly produced via gas-phases reactions with the exception of H$_2$S, which could be produced by the nonthermal desorption of grain-surface JH$_2$S. Among them, CS, SO, and SO$_2$ reach their peak abundances when $A_V$ is around or less than 10 mag, while H$_2$S, CCS, and OCS reach their peak abundances in the inner part of the cloud, which has large $A_V$ and density. Moreover, it can also be seen in Figure 7 that the abundances of SO and SO$_2$ are more sensitive to the physical conditions at certain $A_V$, while other species are much less affected.

Compared with other abundant gas-phase tracers, such as CO, there is a lack of abundant S-bearing molecular tracers in the gas phase for the sulfur chemistry. The abundance of CS reaches $10^{-6}$ in the hot corino condition (Codella et al. 2021), and depletes to $10^{-8}$ in the hot core and dark cloud (Luo et al. 2019; Bulut et al. 2021). In Figure 7, it can be seen that the CS abundance could reach the highest value of $10^{-6}$ at $A_V = 4$ mag. However, the dominant sulfur-carriers above this level are atomic sulfur in the gas phase and JHS and JH$_2$S on the grain surface. The reason is twofold: the initial elemental S abundance is less than that for C, O, and N; and S is heavier than C, O, and N, making it easier to adsorb on the grains.

### 3.2.4. Nitrogen-bearing Molecules

Figure 8 shows the gas-phase N (in empty markers), N$_2$ (in filled markers), and other nitrogen-bearing species as a function of $A_V$. The initial nitrogen is in the neutral atomic form due to its slightly higher ionization potential (14.5 eV) than that of the H atom. It can be seen in Figure 8 that the majority of nitrogen remains in its neutral atomic form when $A_V$ is less than 10 mag, and mostly convert to N$_2$ at higher $A_V$. N$_2$ is not observable at infrared or millimeter-wavelength transitions, but can be estimated by the main production channel of N$_2$H$: N_2 + H$^+ \rightarrow H_2 + N_2H^+$. Womack et al. (1992) estimated a gas-phase N$_2$ abundance of $4 \times 10^{-5}$ through N$_2$H$^+$ under the dark cloud conditions, and suggested gas-phase N$_2$ as the dominant nitrogen-bearing species. In our models, for $A_V > 10$ mag, the N$_2$ abundance varies between $5 \times 10^{-5}$ and $1 \times 10^{-5}$, which is less than 3 times the observational value. N$_2$ is mainly produced by the reaction N + CN $\rightarrow$ C + N$_2$ at earlier times ($\sim 5 \times 10^4$ yr), and by the cosmic-ray desorption of grain-surface JN$_2$ at later times. Two of the destruction pathways of N$_2$ are the reaction N$_2$ + H$_3^+ \rightarrow H_2 + N_2H^+$ and the adsorption onto the grain surface. The production of NH$_3$ also starts from N$_2$. First, N$^+$ is produced by the reaction N$_2$ + He$^+$ $\rightarrow$ N$^+$ + N + He. Then, following the sequence of N$^+$, NH$^+$, NH$_2^+$, and NH$_3^+$ with the reaction of H$_2$, NH$_3^+$ is produced. Finally, NH$_3$ is produced by the reaction NH$_3^+$ $\rightarrow$ e$^- \rightarrow$ H + NH$_3$. The family of cyanopolyynes, HC$_n$N ($n = 3, 5, 7, 9$), are produced by the reaction of CN with hydrocarbons of C$_n$H$_2$ ($n = 2, 4, 6, 8$). Overall, except for N$_2$, it can be seen from Figure 8 that the abundances of most nitrogen-bearing species gradually increase with larger $A_V$ and peak at the highest density. Generally, the nitrogen-bearing species trace the regions with higher $A_V$ and larger $n_H$.

By comparing the gas-phase N$_2$ in Figure 8 with the grain-surface JN$_2$ in Figure 10, it can be seen that the trends for N$_2$ and JN$_2$ are very similar, both having a turning point around an $A_V$ of 4–5 mag. The grain-surface JN$_2$ is mainly produced by...
the grain-surface reaction \( \text{JN} + \text{JNO} \rightarrow \text{JO} + \text{JN}_2 \) and also by gas-phase \( \text{N}_2 \) adsorption. The major consuming channel for \( \text{JN}_2 \) is its cosmic-ray desorption to the gas phase, which is independent of \( A_V \). Thus, the gas-phase \( \text{N}_2 \) and grain-surface \( \text{JN}_2 \) are well coupled through the adsorption and desorption mechanism. By comparing the estimated \( \text{N}_2 \) abundances in the dark clouds and in the warm clouds, which show no difference, Womack et al. (1992) suggested that dust grains may not play an important role in the \( \text{N}_2 \) chemistry. However, according to our above analysis, we suggest that dust grains indeed could play an important role in the \( \text{N}_2 \) chemistry by keeping \( \text{N}_2 \) on the grain surface and releasing it back to the gas phase at a later time.

### 3.2.5. Complex Organic Molecules

COMs, which are defined as carbon-containing molecules with at least six atoms (Herbst & van Dishoeck 2009), represent the advanced complexity during the development of the chemistry. Some COMs, such as \( \text{CH}_3\text{OH} \) and \( \text{CH}_3\text{CHO} \), have been detected in the diffuse clouds toward the Galactic center (Thiel et al. 2017) and in translucent clouds (Turner 1998; Turner et al. 1999). Thiel et al. (2017) estimated the

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**Figure 7.** Abundances of \( \text{S}^+ \), \( \text{S} \), and other S-bearing species in the gas surface and on the grain surface. In the top left panel, \( \text{S}^+ \) is shown by empty markers, while \( \text{S} \) is shown by filled markers. For JHS and JH\(_2\)S, the prefix “J” stands for grain-surface species.
abundances with respect to H2 for CH3OH, CH3CHO, and NH2CHO in the diffuse clouds toward the line of sight of Sagittarius B2 of $8.1 \times 10^{-8}$, $<3.2 \times 10^{-9}$, and $<8.5 \times 10^{-10}$, respectively, at a $\upsilon_{LSR}$ of 9.4 km s$^{-1}$. The fractional abundances with respect to H2 for CH3OH and CH3CHO in translucent clouds are in the range of $10^{-9}$–$10^{-8}$ (Turner 1998; Turner et al. 1999). However, the origin of these COMs in the diffuse and translucent clouds is still under debate. Liszt et al. (2018) argued that the nature of the host gas environment could complicate this situation. Indeed, as suggested in Thiel et al. (2017), the diffuse cloud chemistry could be enriched by the mixing between the dense part and diffuse part of the gas.

Figure 9 shows the modeled abundances of the three COMs as a function of $A_V$. At intermediate $A_V$ (around 5 mag), the modeling CH3OH abundance is consistent with the observations, while CH3CHO and NH2CHO are underproduced. CH3OH is first synthesized on the grain surface and then desorbed into the gas phase by the chemical process. The main

Figure 8. Gas-phase abundances of N, N$_2$, and other nitrogen-bearing species as a function of $A_V$. In the top left panel, N is shown by empty markers, while N$_2$ is shown by filled markers.

Figure 9. Gas-phase abundances of three complex organic molecules as a function of $A_V$. 

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chemical process for the production of gas-phase CH$_3$OH is the chemical desorption of the exothermic surface reactions. Under a grain temperature of $\sim$10 K, thermal desorption is not efficient, and other desorption mechanisms, such as cosmic-ray desorption, also contribute less due to the high desorption energy of grain-surface methanol. The origin of gas-phase NH$_3$CHO is similar. However, CH$_3$CHO is mainly produced by the gas-phase reactions O + C$_2$H$_4$ $\rightarrow$ CH$_3$ + CH$_2$CHO and O + C$_2$H$_5$ $\rightarrow$ H + CH$_3$CHO. The destruction pathways for these COMs are mostly caused by the abundant atomic carbon and the UV photodissociation. The high radiation field in the diffuse and translucent environment is one of the reasons for the low abundances of the COMs. On the one hand, COMs could be dissociated by high-energy photons. On the other hand, the grain-surface chemistry, which is one of the channels that produce the formation of COMs, could also be suppressed by high radiation. Nevertheless, our modeling results show that COMs indeed could be produced at an abundance higher than $10^{-11}$ in the translucent clouds with $A_V$ down to 3 mag.

### 3.2.6. Variation of Grain Ice Composition

Water ice is widely present in dense clouds based on the observations toward the line of sight dense part of clouds toward the background stars (Gibb et al. 2000, 2004). However, there is no strong evidence for the existence of solid-state water in the diffuse–dense transition region (Poteet et al. 2015). Recently, Potapov et al. (2021) shows that water ice could be expected in the diffuse ISM by laboratory experiments. Although the mixture of grain ice mantle compositions is hard to determine, it is interesting to investigate the variation in grain ice compositions under different conditions for the exploration of the grain-surface chemistry and the role of gas–grain interactions. In Figure 10 we show the predicted abundances of grain-surface species as a function of $A_V$. Water ice (JH$_2$O) is the most abundant species when $A_V$ is higher than 4 mag. However, most JH$_2$O are dissociated by UV photons when $A_V$ is less than 4 mag, thereby causing its decrease in the grain ice mantles. Under this condition, the three most abundant ice compositions are JCO$_2$, JCO, and JN$_2$. Among them, JCO$_2$ is the dominant ice composition at low $A_V$ because of the reactions between JCO and JOH and between JO and JHOCO, where JOH is produced by the photodissociation of JH$_2$O. The abundance of JCO has a turning point around 4–5 mag resulting from the competition between its destruction and formation pathways. The destruction pathways of JCO are the reactions with JH and JOH, while the dominant formation pathways of JCO are the UV-photon dissociation and cosmic-ray-induced UV-photon dissociation of grain-surface JCO$_2$. Note that, when $A_V$ is less than 5 mag, the contribution of the gas-phase CO adsorption is unimportant. When $A_V$ is smaller than 5 mag, the abundance of JCO gradually increased because of the increased strength of the UV photons and cosmic-ray-induced UV-photon dissociation of JCO$_2$. On the contrary, starting from the turning point, with the increase in $A_V$ the effect of photodissociation of JCO$_2$ becomes weaker and gas-phase CO adsorption becomes more important, thus leading to the increase in the JCO abundance. After $A_V$ > 10 mag, part of JCO is hydrogenated to produce JHCO, JH$_2$CO, and JCH$_3$OH gradually. It can be seen in Figure 10 that the abundances of JHCO, JH$_2$CO, and JCH$_3$OH are more dependent on $A_V$ and reach their highest values at the largest $A_V$ considered in the models. On the other hand, JH$_2$O, JCO$_2$, JHCOOH, JHCN, and JN$_2$ are generally kept constant when $A_V$ is higher than 4 mag. JHCN and JN$_2$ are produced by the grain-surface reactions JH$_2$ + JCN $\rightarrow$ JH + JHCN and JN + JNO $\rightarrow$ JO + JN$_2$, respectively. They are both the dominant nitrogen-bearing molecules on the grain surface.

The grain ice mantle composition depends on many factors, such as the radiation field and $n_{\text{H}_2}$ density. We show in Figure 11 the development of the grain ice mantle layers as a function of time in four positions at the horizontal line of TMC-1 C and its offset 3, 4, and 5 (see Table 1). It can be seen that the ice layers gradually decrease with the decrease in $A_V$. The ice layers for $A_V$ of 2.2 mag are thicker than those for $A_V$ of 4.8 mag at the time before $10^5$ yr. This is due to the 2 times higher $n_{\text{H}_2}$ density toward the position at $A_V$ of 2.2 mag than that toward the position at $A_V$ of 4.8 mag. We list in Table 3 the most abundant fractional ice composition at these positions. In comparison, we also list the observational values of the fractional ice comparison toward Elias 16 where the location is in the TMC and the dust-embedded young stellar object W33A (Gibb et al. 2000). Water ice is the dominated ice composition at the dense part of the clouds. CO and CO$_2$ ice show comparable fractions in the ice mantles. Meanwhile, the hydrogenated H$_2$CO, CH$_3$OH, NH$_3$, and CH$_4$ ingredients increased the ice composition complex. However, in the diffuse-translucent part of the clouds, with the effect of the changes in physical conditions, such as the radiation field and $n_{\text{H}_2}$ density on the grain ice mantles, the grain ice compositions are greatly altered. Under these conditions, the CO$_2$ ice becomes the dominant ice composition, with H$_2$O, N$_2$, and CO ice as the main ingredients.

### 4. Discussion

In this section, we discuss the discrepancy between the modeling results of large hydrocarbons and sulfur-bearing molecules from their observations.

It can be seen in Figure 2 that hydrocarbons with a number of carbon below 3 are well produced, while large hydrocarbons for the family of C$_n$H$_{2n+2}$ with $n = 4$, 6, 8, are overproduced. Anions are mainly produced by the electron attachment with a neutral species, such as C$_n$H, and are destructed by hydrogen atom addition. The two reaction pathways finally lead to the formation of C$_n$H$_2$, and their rates are rapid under laboratory measurements (Agúndez & Wakelam 2013). It is notable that the abundance of atomic carbon is underproduced by almost 2 orders of magnitude, which means that too much carbon is converted to other carbon-bearing species. The initial donor of carbon is C$^+$, and hydrocarbons grow by the reactions of C$^+$ + C with C$_{n-1}$H$_2$ or C$_{n-1}$H$_2^+$, respectively. As a result, the overproduced large hydrocarbons may indicate the too efficient conversion processes, although we cannot rule out the possibility of the inefficient destruction pathways of large hydrocarbons. In the reaction network, hydrocarbons are mainly dissociated by O or H$_2^+$, or react with C to form larger hydrocarbons. There are also charge exchange reactions in the gas phase, but their effect on the decrease in hydrocarbons is minor. To the best of our knowledge, the charge exchange reactions of hydrocarbons with grains are not well considered in the network; thus their effect on the destruction of hydrocarbons is hard to determine.

The sulfur chemistry is another unsolved problem both in terms of observation and astrochemical modeling. The cosmic value of the sulfur elemental abundance is about $1.5 \times 10^{-5}$. 
For commonly detected sulfur-bearing molecules (such as CS, CCS, SO, and H$_2$S) in dense clouds and other environments, such as diffuse clouds and infrared dark clouds, the abundances are generally on the level of $10^{-9}$ or below (Neufeld et al. 2015; Fuente et al. 2019; Navarro-Almaida et al. 2020; Xie et al. 2021). It is also considered that most sulfur could be depleted onto the dust grains. Observationally, the abundances of solid H$_2$S, SO$_2$, and OCS ice with respect to H$_2$O ice could reach 0.7%, 0.8%, and 0.04%, respectively (Palumbo et al. 1995; Boogert et al. 1997; Jiménez-Escobar & Muñoz Caro 2011). In the dense part of the clouds, our modeling results show that the dominated carrier for sulfur is atomic sulfur in the gas phase ($10^{-6}$–$10^{-7}$ with respect to hydrogen nuclei) and solid HS and H$_2$S on the ice mantles (2% with respect to water ice).

As presented in Section 3.1.1, our model could reproduce 71% of 93 observed species in TMC-1 CP, where 9 out of 20 sulfur-bearing species are out of the 1 order of magnitude criterion. Vidal et al. (2017) reproduced a similar percentage with a total observed species of 61 in which 11 sulfur-bearing molecules are included. To solve the overproduced CS problem, Bulut et al. (2021) considered the reaction CS + O → CO + S with a newly theoretical calculated reaction rate. However, in their modeling result for the abundance of CS, CS

![Figure 10. Abundances of grain-surface species as a function of AV. The prefix "J" stands for grain-surface species.](image-url)
is still overproduced. As can be seen in Figure 2, most overproduced species are carbon-sulfur chains. In the chemical reaction network, sulfur chemistry is well connected with the hydrocarbons, such as the reactions with C\textsubscript{n}H and C\textsubscript{n}H\textsubscript{2} family (Agúndez & Wakelam 2013). This indicates that the overproduced sulfur-bearing species and hydrocarbons may connect with each other. However, the existence of different types of interstellar dust grains could complicate the situation. Unlike the silicate dust grain used in our model, there are also carbonaceous grains and polycyclic aromatic hydrocarbons (PAHs; Draine 2003). The destruction of carbonaceous grains could provide an additional source of carbon elements that may eventually influence the chemistry, and the inclusion of PAHs in the chemistry has been shown to improve the agreement with observations for some species (Wakelam & Herbst 2008; Ge et al. 2020). Further explorations on the puzzling sulfur chemistry and the link between sulfur and hydrocarbons are needed to better understand their formation and destruction pathways in dark clouds.

Last but not least, as mentioned in the Introduction section, the large number of emerged molecules detected in TMC-1 recently challenged the modeling of astrochemistry. Due to the lack of most of these new species in the reaction network, a comprehensive understanding of their evolution is less constrained, and indeed current simple modeling of their formation tends to underproduce their abundances. Thus, a systemic census on the formation and destruction pathways for these newly emerged species will be carried out in future studies.

5. Summary

In this paper, we investigated the chemical variations across the TMC-1 filament from the outer regions to the innermost regions, which represent the transitions from the translucent phase to the dense phase as indicated by the extinction. Three horizontal lines were chosen starting from three emission peaks, which are the cyanopolyynes emission peak (TMC-1 CP), the ammonia emission peak (TMC-1 NH\textsubscript{3}), and the dust continuum peak (TMC-1 C). Their physical parameters were extracted from Fuente et al. (2019), which were used to constrain the physical conditions of our studied regions. Among them, TMC-1 CP is a frequently observed target in the literature where more than 90 molecules have been identified. We divided the identified molecules into four groups by the representative species, which are the C group (hydrocarbons), S group (all the sulfur-containing molecules), N group (nitrile-containing molecules), and O group (the remaining oxygen-containing molecules). Under the above conditions, we first constrained our key chemical parameter (i.e., the initial elemental abundances of carbon and oxygen) by comparison between the observational molecular abundances and the predicted modeling abundances, and determined the evolutionary chemical timescale of TMC-1 CP. We then studied the chemical variations in different groups of molecules as a function of the extinction, and investigated the most
common and abundant grain ice mantle compositions. These results could serve as the template for the study of the transitional regions from the translucent phase to the dense phase of molecular clouds. Finally, we presented and analyzed the chemical evolutions of the tracers in these regions, especially for the grain-surface species that show a distinct difference between the translucent phase and the dense phase.

Our model results can be compared with the observational results from Fuente et al. (2019). The trends of the chemical abundances as a function of $A_V$ for species CO, CS, and SO are successfully reproduced, while for $N_2H^+$, the comparison reaches agreement when $A_V > 10$ mag. Xu & Li (2016) studied the CH across the edge of the TMC where $A_V < 2$ mag, and showed that its abundance keeps nearly constant across that region. Our model shows that the abundance of CH also keeps nearly constant when $A_V > 2$ mag. We conclude that the chemical model is a suitable tool to explore the physicochemical conditions of the clouds. We have presented several other species for the four groups, which could be useful for future studies of the transitional regions, such as the edge of a molecular cloud or the region from the envelope to the inner part of a dense core. For the ice mantle species, the future observations of the James Webb Space Telescope could be essential for the identifications of these grain ice mantle compositions.

We summarize the main conclusions as follows:

1. Our best-fit model for TMC-1 CP could fit 71% observed molecules within 1 order of magnitude, and shows that the evolutionary time of TMC-1 CP is $\sim 5.3 \times 10^5$ yr, which is consistent with the CO depletion timescale found in the molecular cores located in the TMC-1 (Figures 1, 2).

2. The variation in the initial carbon-to-oxygen elemental abundance ratio $C/O$ has different impact on different groups of molecules. Specifically, the C and O group molecules favor a low-C/O condition ($C/O = 0.5$), while the S group molecules seem to favor a high-C/O condition. N group molecules are also affected by the variation in C/O. Although cyanopolyynes ($HC_nN$, where $n = 3, 5, 7, 9$) favor the condition at $C/O = 1.0$, the overall N group molecules could be best fitted by a low C/O of 0.5 (Figures 3, 4).

3. As the molecular cloud evolves from the translucent phase to the dense phase, there is a conversion process for carbon-, oxygen-, nitrogen-, and sulfur-bearing species, i.e., from the atomic form to their main reservoir form. However, the dominated converted form depends on the elements. Atomic carbon and oxygen first convert to CO when $A_V \approx 2$ mag (Figure 6). When $A_V \approx 3-4$ mag, ionic atomic sulfur converts to neutral atomic sulfur, which is the main gas-phase reservoir. Sulfur could also be dephased onto grain surface to form JHS and $\text{H}_2\text{S}$ (“3” stands for grain-surface species) when $A_V$ is larger than 10 mag (Figure 7). The conversion of atomic nitrogen to N$_2$ begins when $A_V$ is larger than 10 mag (Figure 8).

4. COMs, such as CH$_2$OH, CH$_3$CHO, and NH$_2$CHO, could also exist in the translucent gas for $A_V$ down to 3 mag (Figure 9). The main chemical mechanism for the production of CH$_2$OH and NH$_2$CHO is the chemical desorption of the grain-surface reactions, while for CH$_3$CHO, it is directly produced in the gas phase.

5. The grain ice mantle composition has a dependence on $A_V$. H$_2$O ice is the dominant ice composition at $A_V > 4$ mag. CO ice is severely reduced around $A_V$ of 4–5 mag. The composition of CO$_2$ ice keeps nearly constant at $A_V > 4$ mag and is the dominant component when $A_V < 4$ mag. N$_2$ ice tends to be enriched at the low-extinction condition (Figure 10, Table 3).

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