CARBON ISOTOPE AND ISOTOPOMER FRACTIONATION IN COLD DENSE CLOUD CORES

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ABSTRACT

We construct a gas–grain chemical network model which includes carbon isotopes (12C and 13C) with an emphasis on isotopomer-exchange reactions. Temporal variations of molecular abundances, the carbon isotope ratios ([12C/13C]), and the isotopomer ratios ([12C13CX/13C12CX]) of CCH and CCS in cold dense cloud cores are investigated by numerical calculations. We confirm that the isotope ratios of molecules, both in the gas phase and grain surfaces, are significantly different depending on whether the molecule is formed from the carbon atom (ion) or the CO molecule. Molecules formed from carbon atoms have CX/13CX ratios greater than the elemental abundance ratio of [12C/13C]. On the other hand, molecules formed from CO molecules have CX/13CX ratios smaller than the [12C/13C] ratio. We reproduce the observed C13CH/13CCH ratio in TMC-1, if the isotopomer-exchange reaction, 13CCH + H ⇌ C13CH + H + 8.1 K, proceeds with the forward rate coefficient $k_f > 10^{-11}$ cm$^3$ s$^{-1}$. However, the C13CS/13CCS ratio is lower than that observed in TMC-1. We then assume the isotopomer-exchange reaction catalyzed by the H atom, 13CCS + H ⇌ C13CS + H + 17.4 K. In the model with this reaction, we reproduce the observed C13CS/13CCS, CCS/C13CS, and CCS/13CCS ratios simultaneously.

Key words: ISM: abundances – ISM: clouds – ISM: molecules

1. INTRODUCTION

The elemental abundance ratio of $^{12}$C/$^{13}$C in the local interstellar medium (ISM) is 60 (e.g., Langer & Penzias 1993; Lucas & Liszt 1998). The molecular abundance ratio of $^{12}$CX/$^{13}$CX is often assumed to be the same as this elemental ratio. It has been reported, however, that the carbon chain molecules are diluted in $^{13}$C and the ratio varies among molecules; the ratio of HC$_3$N/H$^{13}$CCCN is 79 (Takano et al. 1998), CCS/$^{13}$CCS is 230 ± 130 (Sakai et al. 2007), and CCH/$^{13}$CCH is larger than 250 (Sakai et al. 2010). These ratios should reflect the production pathway of each molecule. In addition, recent observations in TMC-1 indicated that the abundances of the $^{13}$C isotopomers depend on which carbon atom in a molecule is substituted by $^{13}$C. Takano et al. (1998) observed the three $^{13}$C isotopomers of HC$_3$N and found that HCC$^{13}$CN is more abundant than HCC$^{13}$CCN and H$^{13}$CCCN, which indicates that three carbon atoms are not equivalent in HC$_3$N. Takano et al. (1998) suggested that the neutral–neutral reaction of C$_2$H$_2$ + CN is the main formation path to HC$_3$N. Sakai et al. (2007, 2010) reported the abundance ratios of C$^{13}$CS/$^{13}$CCS = 4.2 ± 2.3 and C$^{13}$CH/$^{13}$CCH = 1.6 ± 0.4. Again, these results indicate that two carbon atoms are not equivalent in CCS and CCH. Sakai et al. (2007, 2010) suggested that the neutral–neutral reactions of CH + CS and CH$_2$ + C would significantly contribute to the CCS and CCH formation, respectively. These results indicate that the neutral–neutral reactions might play an important role in the production of such carbon chain molecules. In this way, observations of $^{13}$C species would be useful to investigate chemistry of organic species.

Langer et al. (1984) and Langer & Graedel (1989) constructed theoretical models of the $^{13}$C chemistry in the gas phase. They showed that carbon-bearing species are divided into three groups: CO, HCO*, and the “carbon isotope pool.” CO is $^{13}$C-rich and the “carbon isotope pool” is $^{13}$C-poor. HCO*, on the other hand, can be either $^{13}$C-rich or $^{13}$C-poor. Recently, Woods & Willacy (2009) revisited the carbon isotope fractionation including the adsorption of gaseous molecules onto grain surfaces and grain surface reactions, but they do not distinguish $^{13}$C isotopomers. In addition, temporal evolutions in molecular clouds are not investigated in detail, because they focused on $^{13}$C species in protoplanetary disks.

In this paper, we present a detailed chemical model in cold dense cloud cores to investigate the carbon isotope fractionation and isotopomer fractionation of CCH and CCS. In Section 2, we describe our fiducial model. In Section 3, we show the evolutions of molecular abundances, isotope ratios, and isotopomer ratios in the fiducial model. In Section 4, we compare our results with the observations in TMC-1. We also discuss the dependence of our results on the assumptions of rate coefficients and initial condition of carbon. Since some terms are confusing, we define them here: “carbon isotope ratio” is the abundance ratio of $^{12}$CX/$^{13}$CX and “carbon isotopomer ratio” is the abundance ratio of the $^{12}$C$^{13}$CX/$^{13}$C$^{12}$CX. If a carbon isotopomer ratio deviates from the elemental $^{12}$C/$^{13}$C ratio, we call it “carbon isotope fractionation.” If carbon isotopomer ratio deviates from unity, we call it “carbon isotopomer fractionation.”

2. FIDUCIAL MODEL

2.1. Carbon Isotope Fractionation

There are two processes which fractionate carbon isotopes in molecular clouds: selective photodissociation and isotopomer-exchange reactions.

2.1.1. Selective Photodissociation

Carbon monoxide is photodissociated mostly by line absorption. Because of the high abundance of CO, self-shielding is efficient, especially for $^{12}$CO. Therefore, the $^{12}$CO/$^{13}$CO ratio is enhanced in the very thin surface region ($A_V < 1$ mag; e.g., van Dishoeck & Black 1988). In this study we consider the central regions of molecular cloud cores with $A_V \sim 10$ mag, and hence we do not consider this process in the following sections.
where the vibrational zero-point energy difference is 10 K: Langer et al. (1984) estimated the reaction rate coefficient at the reaction was measured by Watson et al. (1976) at 300 K and the reactants and products, is 35 K. The rate coefficient of this reaction was measured by Yamada et al. (2002). In the case of the sulfur ion, the reaction could be due to the neutral–neutral reaction:

\[
\text{CH + CS} \rightarrow \text{CCS + H},
\]

\[
\text{C} + \text{CH}_2 \rightarrow \text{CCH} + \text{H}.
\]

Two carbon atoms are not equivalent in this neutral–neutral reaction:

\[
\text{12C} + \text{13CH}_2 \rightarrow \text{12C}^{13}\text{CH} + \text{H},
\]

\[
\text{13C} + \text{12CH}_2 \rightarrow \text{13C}^{12}\text{CH} + \text{H}.
\]

If the isotope ratios of the carbon atom and CH$_2$ are different, the isotopomer ratio of CCH deviates from unity.

Similarly, the observed isotopomer fractionation of CCS could be due to the neutral–neutral reaction:

\[
\text{CH + CS} \rightarrow \text{CCS + H},
\]

in which two carbon atoms are not equivalent:

\[
\text{12CH} + \text{13CS} \rightarrow \text{12C}^{13}\text{CS} + \text{H},
\]

\[
\text{13CH} + \text{12CS} \rightarrow \text{13C}^{12}\text{CS} + \text{H}.
\]

In addition, the isotopomer fractionation of CCH might propagate to CCS through the following reactions (Yamada et al. 2002):

\[
\text{CCH} + \text{S} \rightarrow \text{CCS} + \text{H},
\]

\[
\text{S}^+ + \text{CCH} \rightarrow \text{CCS}^+ + \text{H},
\]

\[
\text{CCS}^+ + \text{H}_2 \rightarrow \text{HCCS}^+ + \text{H}.
\]

In reaction (7), the sulfur atom will attack the end carbon atom of CCH, which has the unpaired electron, to form the CCS structure (Yamada et al. 2002). In the case of the sulfur ion, the reaction may occur in a similar way. So, C$^{13}$CS is made from C$^{13}$CH, and C$^{12}$CS is made from C$^{12}$CH through these processes. If these processes are efficient, the C$^{13}$CS/C$^{12}$CS ratio should be less than unity, given that the C$^{13}$CH/13CCH ratio is greater than unity. This is inconsistent with the observation: both the isotopomer ratios of CCH and CCS are greater than unity.

2.2.2. Isotopomer-exchange Reactions

Fractionation by isotopomer-exchange reactions is also possible:

\[
\text{13C}$^{12}$CH + H \rightarrow \text{12C}^{13}\text{CH} + \text{H} + \Delta E,
\]

\[
\text{13C} + \text{12CH}_2 \rightarrow \text{13C}^{12}\text{CH} + \text{H}.
\]

where \(\Delta E\), the zero-point vibrational energy difference of $^{13}$CCH and $^{12}$CCH, is 8.1 K (R. Tarroni 2009, private communication). As a candidate of the isotopomer-exchange reaction of CCS, on the other hand, Sakai et al. (2010) considered the following reaction:

\[
\text{13C}^{12}\text{CS} + \text{S} \rightarrow \text{12C}^{13}\text{CS} + \text{S} + \Delta E,
\]

\[
\text{13C} + \text{12CH}_2 \rightarrow \text{13C}^{12}\text{CH} + \text{H}.
\]

where \(\Delta E\), the zero-point vibrational energy difference of $^{13}$CCS and $^{12}$CCS, is 17.4 K. According to the energy surface calculations, these exchange reactions, (9) and (10), do not have the activation barrier (Y. Osamura 2010, private communication). At low temperature ($T \sim 10$ K), the isotopomer ratios of CCH and CCS can be greater than unity.

### Table 1

| Reaction | \(k\) (cm$^3$ s$^{-1}$) | \(\Delta E\) (K) |
|----------|------------------------|------------------|
| CH + CS → CCS + H | 1.00(−10)$^b$ | ... |
| CH + $^{13}$CS → $^{13}$CCS + H | 1.00(−10) | ... |
| $^{13}$CH + CS → $^{13}$CCS + H | 1.00(−10) | ... |
| CCS$^+$ + H$^+$ → HCCS$^+$ + H | 1.00(−9) | ... |
| $^{13}$CCS$^+$ + H$^+$ → HCC$^{13}$CS$^+$ + H | 1.00(−9) | ... |
| $^{13}$CC$^+$ + CO → $^{13}$CO + C$^+$ | 1.34(−9) | 35 |
| HC$^{13}$O$^+$ + CO → CO + H$^{13}$CO$^+$ | 6.50(−10) | 9 |
| $^{13}$CC$^+$ + H$^+$ → HCC$^{13}$CS$^+$ + H | 1.00(−9) | ... |
| $^{13}$C$^+$ + CO → $^{13}$CO + C$^+$ | 1.34(−9) | 35 |
| HCC$^+$ + H$^+$ → HCC$^{13}$CS$^+$ + H | 1.00(−9) | ... |
| $^{13}$CC$^+$ + S → $^{13}$CS + S | 1.00(−10) | 17.4 |

**Notes.**

$^a$ For exchange reactions \(k\) are the rate coefficients of forward reactions.

$^b$ \(x(−y)\) represents \(x \times 10^{-y}\).
fractionation occurs. In other words, all the isotope ratios are equal to the elemental $^{12}\text{C}/^{13}\text{C}$ ratio and all the isotopomer ratios are unity.

Second, we include the gas phase reactions in Table 1 referring to the discussion in Section 2.2. The rate coefficients of these reactions are not measured in the laboratory. So, we assume that the rate coefficients are $1 \times 10^{-10}$ cm$^3$ s$^{-1}$ for neutral–neutral reactions and $1 \times 10^{-9}$ cm$^3$ s$^{-1}$ for ion–neutral reactions. The dependence of our results on these rate coefficients is discussed in Section 4.3.

Finally, we modify the branching ratios of proton transfer reactions and electron recombination reactions which break the C–H bond, such as

$$H^{12}C^{12}CS + e \rightarrow 12C^{12}CS + H,$$

$$H^{12}C^{13}CS + e \rightarrow 12C^{13}CS + H,$$

$$H^{12}C^{13}CS^+ + e \rightarrow 13C^{12}CS + H.$$
Figure 1 shows the evolution of the major ice mantle species. H$_2$CO and CH$_3$OH are the most abundant organic species in ice mantles. They are formed from the carbon atom at $t < 2 \times 10^5$ yr and from CO at later times.

Figure 1 (upper panels) shows the evolution of the major ice mantle species. H$_2$CO and CH$_3$OH are the most abundant organic species in ice mantles. They are formed from the carbon atom at $t < 2 \times 10^5$ yr and from CO at later times.

Figure 1 (lower panels) shows the evolution of the isotopic ratios of the ice mantle species. Carbon atoms and carbon monoxides in the gas phase are adsorbed and form more complex species by grain surface reactions. Before $10^5$ yr, the isotopic ratio of carbon atoms on grain surfaces is almost the same as in the gas phase. Carbon monoxide, on the other hand, is directly absorbed on grain surfaces and is also formed by the grain surface reactions of the carbon-bearing species. Then, the isotopic ratio of CO on grain surfaces is slightly different from that in the gas phase. The isotopic ratios of ice mantle species depend mainly on whether the species are formed from the carbon atom or the CO molecule; the isotopic ratio is larger than 60 if the species are formed from the C atom, while the ratio is smaller than 60 if the species are formed from CO. For example, CH$_3$OH is formed from the carbon atom and its isotopic ratio is 81 at $t = 2 \times 10^5$ yr. After $2 \times 10^5$ yr, CH$_3$OH is formed from the CO molecule and the isotopic ratio decreases to 53 at $10^6$ yr, which is almost the same as the isotopic ratio of CO. HCOOH is an exception. It is formed from HCO$^+$ in the gas phase and adsorbed onto the grain surfaces. The isotopic ratio of HCOOH is similar to that of HCO$^+$ in the gas phase. Isotopic ratios of ice species in higher ($5 \times 10^5$ cm$^{-3}$) and lower ($5 \times 10^3$ cm$^{-3}$) density models are listed in Table 4.

Boogert et al. (2000, 2002) found that the solid CO$_2$/H$_2$O ratio is similar to the solid CO/O ratio toward NGC 7538 IRS 9 and suggested that CO$_2$ is formed from CO on grain surfaces, rather than from the carbon atom in the gas phase. In our model, CO$_2$ is formed in the gas phase via the reaction of an O atom with HCO, which is formed from carbon atom, and adsorbed onto grain surfaces. Then, the isotopic ratio of CO$_2$ is similar to that of the carbon atom. However, if we use the modified rates method (e.g., Ruffle & Herbst 2000), which artificially slows down the surface diffusion rate of the hydrogen atom, CO$_2$ is formed from CO on grain surfaces via the reaction of CO$_2$+O (Aikawa et al. 2005). In this case, the isotopic ratio of CO$_2$ ice at $t > 2 \times 10^5$ yr should be closer to that of CO ice just like H$_2$CO and CH$_3$OH.

It should be noted that the observed isotopic ratio of CO$_2$ ice varies with lines of sight. The solid CO$_2$/H$_2$O and CO$_2$/H$_2$O ratios toward NGC 7538 IRS 9 are actually $71 \pm 15$ and $80 \pm 11$, respectively (Boogert et al. 2000, 2002). The isotopic ratio of CO$_2$ is similar to or slightly higher than that of CO. On the other hand, toward NGC 2264 IRS1, Langer & Penzias (1990) found the gas C$^{13}$O/C$^{18}$O ratio is 56 $\pm$ 3 and Gibb et al. (2004) found the solid CO$_2$/H$_2$O ratio is 131 $\pm$ 21. The isotopic ratio of CO$_2$ ice is higher than that of CO gas by a factor of 2.3, assuming that the carbon isotope fractionation of $^{18}$O species is $10^5$ cm$^{-3}$. The evolution is in general faster at higher densities. Since we are interested in carbon-bearing species, we compare isotopic ratios of these molecules at the time of peak carbon chain abundance: $1 \times 10^5$, $2 \times 10^4$, and $4 \times 10^3$ yr for densities of $5 \times 10^3$, $5 \times 10^4$, and $5 \times 10^5$ cm$^{-3}$, respectively. We found that the isotopic ratios do not significantly depend on density. For example, the CO$_2$/H$_2$O ratio at the selected time is 83, 81, and 80, and the CS/H$_2$S ratio is 83, 92, and 108 for densities of $5 \times 10^3$, $5 \times 10^4$, and $5 \times 10^5$ cm$^{-3}$, respectively. The isotopic ratios of other species in each density model are listed in Table 3.
similar to that of $^{16}$O species (e.g., Langer et al. 1984). In our model, in which CO$_2$ is mainly formed in the gas phase and adsorbed onto grain surfaces, such high isotope ratios of CO$_2$ ice relative to that of CO ice (gas) are realized at $10^5$ yr in the model with $n_H_2 = 5 \times 10^5$, $5 \times 10^6$, and $5 \times 10^7$ cm$^{-3}$.

### 3.2. Isotopomer Ratios

#### 3.2.1. CCH

Figure 3(a) shows the temporal evolution of the assorted species relevant to the isotopomer fractionation of CCH and CCS. Figure 3(b) shows the C$^{13}$CH/$^{13}$CCH ratio. The isotopomer ratio is significantly enhanced in the fiducial model (solid line). In order to investigate whether the isotopomer fractionation of CCH is caused by (1) formation reactions or (2) isotopomer-exchange reactions, we performed a calculation without the exchange reaction (9) (dashed line in Figure 3(b)). It is clear that isotopomer fractionation is mostly due to the exchange reaction.

Figure 4 shows the major formation and destruction paths of CCH isotopomers. Reactions (3) and (4) are the dominant formation reactions until $10^4$ yr. The isotopomer ratio of CH$_2$ is larger than that of carbon atoms, and hence the isotopomer ratio is lowered. After $10^4$ yr, on the other hand, CCH is mainly produced from the destruction of larger species (e.g.,
C$_3$H$_2$) by the oxygen atom and electron recombinations of symmetrical species (e.g., C$_2$H$_3$). These reactions tend to make the isotopomer ratio of CCH unity, since they form the same amount of the CCH isotopomer: C$^{13}$CH and $^{13}$CCH. Therefore, without the exchange reaction (9), the isotopomer ratio becomes almost unity in the model.

In our model, we do not distinguish isotopomers in species with more than four carbons. We checked if this simplification affects our results. We performed calculations without these large carbon chains (more than four carbon atoms) and the exchange reaction (9), and confirmed that the isotopomer ratio of CCH is as low as the dashed line in Figure 3(b).

In the model with the exchange reaction, the isotopomer ratio increases with time in a few $10^3$ yr as the electron abundance decreases. Then, the ratio gradually decreases as the H atom abundance decreases by adsorption and subsequent grain surface reactions. At several $10^4$ yr, the ratio starts to increase again by the adsorption of oxygen atoms. After $3 \times 10^5$ yr, it reaches nearly the equilibrium ratio of 2.2 ($k_i/k_r$).

Since the H atom abundance is an important factor for the efficiency of the exchange reaction (9), we briefly discuss the formation and destruction of H atoms in dense cloud cores (Figure 3(a)). Before $10^4$ yr, the primary sources of the H atom are the reactions of hydrocarbons, such as the recombination of CH$_2^+$ and the reaction of CH + O, and the destruction is by adsorption on grain surfaces followed by subsequent hydrogenation reactions, such as H + OH. At $t > 10^4$ yr, H atoms are mainly formed by cosmic-ray-induced photodissociation of hydrogen molecules. At this stage the absolute abundance of the H atom is $\sim 1$ cm$^{-3}$ independent of the gas density. We also checked the dependence of our results on the initial H atom abundance; if the initial abundance is lowered by an order of magnitude, the isotopomer ratio varies only slightly.

Figure 5 shows density dependence of the C$^{13}$CH/$^{13}$CCH ratio. As the density increases, both the abundances of electron and H atom decrease. While the electron abundance is proportional to $n_{H_2}^{-0.5}$, the H atom abundance is proportional to $n_{H_2}^{-1}$. Then, the peak isotopomer ratio decreases with density.

The isotopomer fractionation also affects the isotope ratios, i.e., the CCH/$^{13}$CCH and CCH/C$^{13}$CH ratios (Figure 6). Reaction (9) enhances $^{13}$C in C$^{13}$CH, while it dilutes $^{13}$C in $^{13}$CCH.
The isotopomer ratio reaches a maximum of about 1.2 by reaction (10) at $3 \times 10^4$ yr. Since carbon chain molecules are abundant in n = 10^4–10^5 cm$^{-3}$, the abundances of carbon chain molecules, such as HC$_3$N, reach their maxima of carbon chain molecules, such as HC$_3$N, reach their maxima at 2 $\times$ 10$^4$ yr. Since carbon chain molecules are abundant in TMC-1, we compare the obtained molecular abundances and isotopic isotope and isotopomer ratios in the fiducial model, whereas the dashed line shows the ratio in the model without isotopomer fractionation.

For comparison, the dashed line in Figure 6 shows the isotope ratios of CCH in the model without the isotopomer fractionation: the model without reactions (3)–(6), (9), and (10).

### 3.2.2. CCS

Figure 7 shows the temporal evolution of the C$^{13}$CS/$^{13}$CCS ratio. The isotopomer ratio of CCS is lower than unity in the model without the exchange reaction (10) (dashed line). Reactions (5) and (6) are not the main formation reactions of C$^{13}$CS and $^{13}$CCS in our model. Instead, CCS is mainly formed by the electron recombination of larger ions, such as HC$_2$S$^+$ (Figure 4). These reactions tend to make the isotopomer ratio of CCS unity. Reactions (7) and (8) decrease the isotopomer ratio of CCS, because the isotopomer ratio of CCH is larger than unity. In the fiducial model (solid line), the isotopomer ratio is lower than unity except for very limited periods. The isotopomer ratio reaches a maximum of about 1.2 by reaction (10) at $3 \times 10^4$ yr. Figure 8 shows the density dependence of the C$^{13}$CS/$^{13}$CCS ratio. Although the peak isotopomer ratio increases with density, the maximum ratio is 1.8, which is much lower than observed. Unlike CCH, the exchange reaction (10) is inefficient, because the sulfur atom is less abundant than the hydrogen atom by three orders of magnitude.

### 4. DISCUSSION

#### 4.1. Comparisons with Observations of TMC-1

The gas density in TMC-1 is 10$^4$–10$^5$ cm$^{-3}$ (Pratap et al. 1997). In the model with $n_{H_2} = 5 \times 10^4$ cm$^{-3}$, the abundances of carbon chain molecules, such as HC$_3$N, reach their maxima at $2 \times 10^4$ yr. Since carbon chain molecules are abundant in TMC-1, we compare the obtained molecular abundances and isotopic and isotopomer ratios in the fiducial model at $2 \times 10^4$ yr to the observed values in TMC-1.

Pratap et al. (1997) made maps along the TMC-1 ridge and determine the column densities of C$^{18}$O and CCH. The molecular abundance of CCH in TMC-1 is $5.7 \times 10^{-10}$ to $4.0 \times 10^{-9}$, assuming a C$^{18}$O/H$_2$ ratio of $1.7 \times 10^{-7}$ (Ferriking et al. 1982). In our model, we obtain the abundance of CCH to be...
3.0 × 10⁻⁹, which is in reasonable agreement with the observed value.

In the fiducial model, we obtain the CCH/¹³CCH, CCH/²⁴C₁₃CH, and ²⁴C₁³CH/¹³CCH ratios to be 99, 63, and 1.6, respectively, at 2 × 10⁴ yr. The observed CCH/¹³CCH and CCH/²⁴C₁₃CH ratios are higher than 170 and 250, respectively (Sakai et al. 2010). The average isotope ratio, which is calculated by

\[ \frac{2 \times \text{CCH}}{\text{C}^{13}\text{CCH} + \text{C}^{13}\text{CCH}} \]

is higher than 200 and is three times higher than our model. Additional isotope-exchange reactions, which are currently unknown, may be needed to reproduce the observed values. On the other hand, the observed C¹³CH/¹³CCH ratio is 1.6 ± 0.4 (Sakai et al. 2010), which is in reasonable agreement with our model. Therefore, the exchange reaction (9) can account for the isotopomer fractionation of CCH.

We obtain the CCS/¹³CCS, CCS/¹³C₁₃S, and ¹³C₁₃S/²⁴C₁₃S ratios to be 84, 76, and 1.1, respectively, in the fiducial model at 2 × 10⁴ yr. The observed CCS/¹³CCS, CCS/¹³C₁₃S, and ¹³C₁₃S/²⁴C₁₃S ratios are 230 ± 130, 54 ± 5, and 4.2 ± 2.3, respectively (Sakai et al. 2007). The average isotope ratio is 87, which is in good agreement with our model results. But our model underestimates the isotopomer fractionation. We discuss this problem in the next section.

4.2. Exchange Reactions of CCS

The isotopomer-exchange reaction (10) is not efficient enough to account for the observed isotopomer ratio of CCS, because of the low abundance of sulfur atoms. Since the reactant is not necessarily the sulfur atom for the exchange reaction, we consider a possibility of the following neutral–neutral reaction:

\[ ^{13}\text{C}^{12}\text{CS} + \text{H} \rightarrow ^{12}\text{C}^{13}\text{CS} + \text{H} + \Delta E , \]  

(11)

where \( \Delta E \) is 17.4 K. This can be regarded as a catalytic reaction by the hydrogen atom. According to the quantum chemical calculation by Yamada et al. (2002), reaction (11) does not have the activation barrier. It could be more effective than reaction (10), because the hydrogen atom is more abundant than the sulfur atom. Since the rate coefficients of reaction (11) has not been measured or calculated, we simply assume that the forward rate coefficient is \( 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \), which is a typical collisional rate coefficient between neutral species. Figure 9(a) shows the temporal evolution of the isotopomer ratio of CCS in the model with the exchange reaction (11). The ratio is significantly enhanced in comparison with the model in Figures 7 and 8 and reaches nearly the equilibrium ratio of 5.7 (\( k_f/k_r \)) at a few 10⁴ yr. After several 10⁴ yr, CCS abundance decreases by about two orders of magnitude (Figure 3(a)). The abundance of S-bearing molecular ions, such as HCCS⁺, decreases only by an order of magnitude, because H₂S abundance is enhanced by the CO depletion. Then the exchange reaction (11), whose efficiency is proportional to the CCS abundance, becomes less effective than ion–molecule reactions, and the isotopomer ratio decreases to 4.1. Our model with reaction (11) can reasonably explain the observed isotopomer ratio.

The isotopomer fractionation also affects the isotopomer ratios, CCS/¹³CCS and CCS/¹³C₁₃S (Figure 9(b)). ¹³C is significantly diluted in ¹³CCS, and the CCS/¹³CCS ratio is higher than 200 in several 10⁴ yr. On the other hand, the CCS/¹³C₁₃S ratio is lower than 60. At 2 × 10⁴ yr, the CCS/¹³CCS and CCS/¹³C₁₃S ratios are 263 and 47, respectively, which are in reasonable agreement with the observed isotope ratios. Hence, reaction (11) is a possible culprit for the isotopomer fractionation of CCS.

4.3. Dependences on Rate Coefficients of Isotopomer-exchange Reactions

In the previous sections, we assumed that the forward reaction rate coefficients of the isotopomer-exchange reactions are all \( 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \), which is a typical collisional rate coefficient between neutral species. However, it is not obvious whether the actual exchange reactions proceed at the collisional rate. For example, the rate coefficient of the similar type of reactions, such as HNC + H → HC₃N + H, is assumed to be \( 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \) in our model (e.g., Garrod & Herbst 2006). In particular, reaction (11) requires the rearrangement of the order of the carbon nuclei in the chain through the transient cyclic isomers (Yamada et al. 2002). Although the reaction is exothermic, the efficiency of reaction (11) might be low. Hence, we investigate the dependence of the isotopomer ratios on the rate coefficients of reactions (9) and (11). Figure 10 shows the temporal evolution of the isotopomer ratios of (a) CCH and (b) CCS. The forward reaction rate coefficients are \( 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) (solid line), \( 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \) (dashed line), and \( 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) (dotted line).
We can see that the forward reaction rate coefficients should be larger than $1 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$ to account for the observed isotopomer ratios by the exchange reactions (9) and (11). Laboratory measurements, as well as more detailed theoretical calculations of these isotopomer-exchange reactions, are highly desirable.

4.4. Initial Condition of the Carbon

So far, we have assumed that all the carbon initially exists as carbon ions. This assumption is the most favorable for the carbon isotope fractionation, because the isotope-exchange reaction (1) becomes efficient. Here, we investigate the dependencies of isotope ratios on the initial condition of the carbon.

We performed calculations with two different initial conditions: (1) half of the carbon exists as atomic carbon, and (2) all the carbon is in atomic form. In the former case, the evolution of isotope ratios in the gas phase is very similar to the fiducial model, because the abundances of major carbon-bearing species are almost the same as the fiducial model after $10^5$ yr. Figure 11 shows the evolutions of (a) molecular abundances and (b) isotope ratios in the gas phase for the latter case: all the carbon is initially atomic carbon. The molecular abundances and isotope ratios are different from the fiducial model before $10^5$ yr, but they approach to the fiducial model after a few $10^5$ yr. The abundances of C, C+, and CO are similar to those in the fiducial model after $10^5$ yr. The isotope ratio of CO is nearly 60 before $10^5$ yr, since the abundance of C+ is small. After $10^5$ yr the ratio slightly decreases: $^{12}\text{CO}^{13}\text{CO} = 56$ at $10^6$ yr. On the other hand, the isotope ratio of C+ is as high (>60) as in the fiducial model, since the abundance of CO is smaller than in the fiducial model only by an order of magnitude. The isotope ratio of the carbon atom is nearly 60 before $10^5$ yr. After $10^5$ yr the ratio becomes greater than 60 because of the neutralization of the carbon ion. “Carbon isotope pool” species are mostly produced from the carbon atoms, then their isotope ratios are similar to that of the carbon atom. In this way, the carbon isotope fractionation occurs by the isotope-exchange reactions after $10^5$ yr, even if all the carbon is initially in the carbon atom. These results suggest that isotope fractionation in early times does not much affect the isotope ratios after $10^5$ yr. In order to account
for the isotope fractionation at the period of peak carbon chain abundances ($t \sim 2 \times 10^4$ yr), however, some fraction of carbon should be carbon ions initially.

4.5. Summary

We constructed a gas–grain chemical network model that includes carbon isotopes and isotopomers in order to investigate the evolution of molecular abundances, the carbon isotope ratios, and the isotopomer ratios of CCH and CCS in cold dense cloud cores. The principal results are follows.

1. We confirm that the isotope ratios of molecules, both in the gas phase and on grain surfaces, mostly depend on whether the species is formed from the carbon atom (ion) or the CO molecule; the isotope ratio is larger than the elemental abundance ratio of $^{12}$C/$^{13}$C if the species is formed from the carbon atom, while the ratio is smaller if the species is formed from the CO molecule.

2. There are two possible processes of isotopomer fractionation: (1) the formation pathways of the species and (2) the exchange of the $^{13}$C position by isotopomer-exchange reactions. We reproduce the observed isotopomer ratio C$^{13}$CH/13CCH by considering the isotopomer-exchange reaction: $^{13}$CCH + H $\rightarrow$ C13CH + H + 8.1 K, if this reaction proceeds with the forward rate coefficient $k_f > 10^{-11}$ cm$^3$ s$^{-1}$. The isotope ratio is underestimated in our model, which is left for future studies.

3. We reproduce the observed C$^{13}$CS/13CCS, CCS/C13CS, and CCS/13CCS ratios simultaneously by considering the isotopomer-exchange reaction: 13CCS + H $\rightarrow$ C13CS + H + 17.4 K, if this reaction proceeds with the forward rate coefficient $k_f > 10^{-11}$ cm$^3$ s$^{-1}$.

4. In conclusion, isotopomer fractionation of CCH and CCS can be due to isotopomer-exchange reactions. Laboratory measurements and detailed quantum calculations of these isotopomer-exchange reactions are highly desired.

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