

Observations of ^{13}C isotopomers of HC_3N and HC_5N in TMC-1: evidence for isotopic fractionation

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Abstract. The ^{13}C substitutions of HC_3N (H^{13}CCCN , HC^{13}CCN , and HCC^{13}CN) were observed in TMC-1 using the $J = 2 - 1$, $4 - 3$, and $5 - 4$ rotational transitions at 18, 36, and 45 GHz, respectively. The spectral lines of HCC^{13}CN are stronger than those of HC^{13}CCN in all observed transitions, while the spectral lines of HC^{13}CCN and H^{13}CCCN show similar intensity. These differences in the intensities are most probably due to ^{13}C isotopic fractionation in the formation process of HC_3N . The abundance ratios are 1.0:1.0:1.4 for $[\text{H}^{13}\text{CCCN}] : [\text{HC}^{13}\text{CCN}] : [\text{HCC}^{13}\text{CN}]$ at the cyanopolyne peak in TMC-1: the ^{13}C isotope is concentrated in a carbon atom adjacent to the nitrogen atom. Based on these observational results, the production mechanism of HC_3N was discussed. As a result, the formation reactions between a hydrocarbon molecule with two carbon atoms (e.g. C_2H_2) and a molecule with a ^{13}C enriched CN group can explain ^{13}C isotopic fractionation: a neutral-neutral reaction between C_2H_2 and CN is probably most important. The ratio of the contributions of two types of the HC_3N formation reactions which can and cannot produce ^{13}C isotopic fractionation is discussed. In addition, the ^{13}C isotopic species of HC_5N ($\text{HC}^{13}\text{CCCCN}$ and $\text{HCCCC}^{13}\text{CN}$) were also observed at the cyanopolyne peak in TMC-1 using the $J = 9 - 8$ rotational transitions at 23.7 GHz. The intensity of $\text{HCCCC}^{13}\text{CN}$ is marginally stronger than that of $\text{HC}^{13}\text{CCCCN}$. Furthermore, the $(J, K) = (2, 2)$ emission of NH_3 was simultaneously observed with the ^{13}C isotopic species of HC_5N . With the additional observation of the $(J, K) = (1, 1)$ emission of NH_3 , the rotational temperature between the (1,1) and (2,2) levels, and the column

density of NH_3 are determined for the cyanopolyne peak in TMC-1.

Key words: molecular processes – ISM: abundances – ISM: molecules – ISM: individual objects: TMC-1 – Radio lines: ISM

1. Introduction

The carbon chain molecules are well known due to their large abundances in cold dark clouds (e.g. Benson & Myers 1983; Suzuki et al. 1992) and in some carbon-rich circumstellar envelopes (e.g. Jewell & Snyder 1984; Sopka et al. 1989; Fukasaku et al. 1994). About 40% of interstellar molecules are classified as carbon chain molecules. The study of these molecules is, therefore, important to understand chemical processes in space. Several formation mechanisms for the carbon chain molecules have been proposed. For example, Schiff & Bohme (1979) and Mitchell et al. (1979) proposed to explain the carbon chain growth by C_2 units: C_2H_2^+ or C_2H_2 . On the other hand, Suzuki (1983) proposed that C^+ , which was produced by interstellar ultraviolet radiation, plays an important role for the carbon chain formation.

Given these possibilities, we have been obtaining observational information on the mechanism of carbon chain formation. One observational approach is to study ^{13}C isotopic fractionation in the carbon chain molecules. If ^{13}C isotopic fractionation is found, we can discuss the mechanisms of fractionation and the origin of the fractionated carbon. Such discussions are quite useful to study formation mechanisms.

The most widely accepted mechanism of isotopic fractionation is via isotope exchange reactions (Watson 1974). In case

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of the ^{13}C isotope in CO, the isotope exchange reaction is as follows:



which contributes to the concentration of the ^{13}C isotope in CO. The value of ΔE corresponds to 35 K (Watson et al. 1976). As shown above, isotope exchange reactions with slight exothermicity for the forward reaction cause isotopic fractionation, thus introducing the temperature dependence. Isotopic fractionation is, therefore, expected to be larger in low temperature regions such as dark clouds (Watson 1976).

In the solar neighborhood, the interstellar carbon isotopic ratio ($^{12}\text{C}/^{13}\text{C}$) is ~ 70 (see Wilson & Rood 1994). This value is based on CH^+ isotope measurements toward ζ Oph (Stahl et al. 1989; Crane et al. 1991; Stahl & Wilson 1992; Hawkins et al. 1993). The CH^+ isotope ratios are not affected by fractionation since this molecule requires very high temperatures for formation.

The most prominent series of carbon chain molecules is the cyanopolyynes, $\text{H} - (\text{C} \equiv \text{C})_n - \text{C} \equiv \text{N}$ ($n = 0, 1, 2, 3, 4,$ and 5). The second member of this series, HC_3N , is a key molecule to understand the cyanopolyne formation, because HC_3N is produced at early stage of the cyanopolyne growth. Therefore, the abundances of the ^{13}C isotopic substitutions, that is, isotopomers of HC_3N (H^{13}CCCN , HC^{13}CCN , and HCC^{13}CN) are particularly interesting to study ^{13}C isotopic fractionation. In addition, spectra with high signal-to-noise ratios can be obtained for these isotopomers, because HC_3N is one of the most abundant carbon chain molecules.

The ^{13}C isotopomers of HC_3N were first detected by Gardner & Winnewisser (1975) in Sgr B2. Since then several observations have been carried out about the ^{13}C isotopic species mainly with the interest in ^{13}C isotopic fractionation. In Sgr B2, Churchwell et al. (1977) observed the $J = 1 - 0$ transitions of the three isotopic species and found that the intensity of the H^{13}CCCN line was stronger than those of HC^{13}CCN and HCC^{13}CN . However, Wannier & Linke (1978) reported no differences in intensities among the three ^{13}C isotopic species from their observations using the $J = 9 - 8$ transitions in Sgr B2 and Ori KL. Further observations (Olofsson et al. 1982; Johansson et al. 1984, 1985; Cummins et al. 1986; Mangum et al. 1988; Kahane et al. 1988; Turner 1991) also found no significant differences in intensities among the three ^{13}C isotopomers in Sgr B2, Ori KL, and IRC+10216.

However, these sources are rather hot (e.g. $T_K = 175$ K for Sgr B2, Hüttemeister et al. 1995), while from the reaction (1), larger isotopic fractionation is expected in low temperature regions. Since Taurus Molecular Cloud-1 (TMC-1) is a cold dark cloud ($T_K = 10 \pm 1$ K near NH_3 peak, Töle et al. 1981; see also Sect. 3.5) with strong emission lines of carbon chain molecules, this source is suitable for observations of ^{13}C isotopic fractionation in HC_3N . Mangum et al. (1988) have already observed the three ^{13}C isotopic species of HC_3N using the $J = 1 - 0$ transitions in this object. But the signal-to-noise ratios of their spectra are not sufficient to obtain information about isotopic fractionation.

In addition, the relative abundances among the ^{13}C isotopic species of a longer cyanopolyne HC_5N are important to understand the transfer of ^{13}C isotopic fractionation by carbon chain growth. They were already detected in TMC-1 by Takano et al. (1990), but the signal-to-noise ratios are not sufficient for the present purpose.

Therefore we observed the three ^{13}C isotopomers of HC_3N and two ^{13}C isotopomers of HC_5N ($\text{HC}^{13}\text{CCCCN}$ and $\text{HCCCC}^{13}\text{CN}$) with higher signal-to-noise ratio toward TMC-1. As a result, ^{13}C isotopic fractionation was clearly found for HC_3N and marginally found for HC_5N . The preliminary result of the present study was already reported by Takano et al. (1992). As far as we know, there is only one article about ^{13}C isotopic fractionation in carbon chain molecules except HC_3N : Saleck et al. (1994) reported a possible abundance difference between ^{13}CCH and C^{13}CH in the Orion A ridge, although there is a remaining uncertainty due to the calibration.

2. Observations

2.1. Observations of HC_3N

The HC_3N observations were carried out with the 45-m telescope of Nobeyama Radio Observatory (NRO) in 1988 March and 1992 April. The source observed was the cyanopolyne peak in TMC-1 (R.A. = $4^{\text{h}}38^{\text{m}}38.^{\text{s}}6$, Decl. = $25^{\circ}35'45''$, epoch 1950.0). Two of the ^{13}C isotopomers, HC^{13}CCN and HCC^{13}CN , were measured using the $J = 2 - 1$, $4 - 3$, and $5 - 4$ rotational transitions at 18, 36, and 45 GHz regions, respectively. The other ^{13}C isotopomer, H^{13}CCCN , was observed using the $J = 4 - 3$ rotational transition in 35 GHz region. The observations of the $J = 4 - 3$ transitions of the three ^{13}C isotopic species were carried out simultaneously with the same receiver to minimize calibration and pointing errors. In addition, the most abundant isotopomer, HC_3N , was measured using the $J = 2 - 1$, $4 - 3$, $5 - 4$, and $10 - 9$ rotational transitions at 18, 36, 45, and 91 GHz, respectively. In the case of the $J = 5 - 4$ and $10 - 9$ transitions of HC_3N and the $J = 5 - 4$ transitions of HC^{13}CCN and HCC^{13}CN , two other positions in TMC-1 were observed in addition to the cyanopolyne peak. These were near the ammonia peak (R.A. = $4^{\text{h}}38^{\text{m}}16.4^{\text{s}}$, Decl. = $25^{\circ}41'45''$, that is, Δ R.A. = $-5'$, Δ Decl. = $6'$ from the cyanopolyne peak) and a southeastern offset from the cyanopolyne peak (at $4^{\text{h}}38^{\text{m}}47.5^{\text{s}}$, $25^{\circ}33'45''$, or an offset Δ R.A. = $2'$, Δ Decl. = $-2'$). In Table 1 we list the isotopomer observed, the rest frequencies, receivers, system noise temperatures, main beam efficiencies, and beam sizes.

The observations were made in the position switching mode, using a single reference position (Δ R.A. = $12'$, Δ Decl. = $12'$). The chopper wheel method was used for the intensity calibration. The backend was a bank of eight high-resolution acousto-optical spectrometers with the bandwidth of 40 MHz and the frequency resolution of 37 kHz. The corresponding velocity resolutions are 0.62, 0.31, 0.25, and 0.12 km s^{-1} at 18, 36, 45, and 91 GHz, respectively. The V_{LSR} of TMC-1 was assumed to be 5.85 km s^{-1} . The pointing was checked every two hours by ob-

Table 1. Observed species and observational parameters

Transition	Species	Frequency ^a (MHz)	Relative intensity ^b	Date	Receiver ^c	T _{sys} ^d (K)	η_B^e	Beam size ($''$)						
Nobeyama 45 m telescope:														
$J = 2 - 1$	HC^{13}CCN	18119.0294(48) ($F = 2 - 1$)	0.250	1992 April	(1)	120	0.80	105						
		18119.1215(49) ($F = 3 - 2$)	0.467											
	HCC^{13}CN	18120.7731(18) ($F = 2 - 1$)	0.250											
		18120.8653(18) ($F = 3 - 2$)	0.467											
	HC_3N	18194.9206(8) ($F = 2 - 2$)	0.083											
		18195.3176(6) ($F = 1 - 0$)	0.111											
		18196.2183(5) ($F = 2 - 1$)	0.250											
		18196.3119(7) ($F = 3 - 2$)	0.467											
$J = 4 - 3$	H^{13}CCCN	35267.3162(75) ($F = 3 - 2$)	0.238	1992 April	(2)	400–500	0.78	53						
		35267.4077(73) ($F = 4 - 3$)	0.313											
		35267.4401(73) ($F = 5 - 4$)	0.407											
	HC^{13}CCN	36237.8623(87) ($F = 3 - 2$)	0.238											
		36237.9544(87) ($F = 4 - 3$)	0.313											
		36237.9869(87) ($F = 5 - 4$)	0.407											
	HCC^{13}CN	36241.3504(33) ($F = 3 - 2$)	0.238											
		36241.4425(33) ($F = 4 - 3$)	0.313											
		36241.4751(33) ($F = 5 - 4$)	0.407											
	HC_3N	36390.8878(13) ($F = 4 - 4$)	0.021											
		36392.2380(10) ($F = 3 - 2$)	0.238											
		36392.3316(10) ($F = 4 - 3$)	0.313											
		36392.3654(11) ($F = 5 - 4$)	0.407											
	$J = 5 - 4$	HC^{13}CCN	45297.345(10) ^f						0.973	1988 March	(3)	300	0.65	42
			HCC^{13}CN						45301.708(3) ^f					
		HC_3N	45492.1104(16) ($F = 4 - 4$)						0.013					
45490.307(4) ($F = 4 - 3, 5 - 4, 6 - 5$) ^f			0.973											
45488.8386(16) ($F = 5 - 5$)			0.013											
$J = 10 - 9$	HC_3N	90978.9933(21)	0.993	1988 March	(4)	450	0.55	21						
Effelsberg 100 m telescope:														
$J = 9 - 8$	$\text{HC}^{13}\text{CCCCN}$	23718.325 ^g	0.991	1992 April	(5)	70	0.34	43						
		$\text{HCCCC}^{13}\text{CN}$	23727.162 ^g						0.991					
$(J, K) = (1, 1)$	NH_3	23694.495 ^h	0.500											
$(J, K) = (2, 2)$	NH_3	23722.633 ^h	0.796											

^a Lafferty & Lovas (1978). The value in parentheses is the estimated uncertainty and applied to the last significant digits.

^b The relative intensity in each rotational or inversion transition. The sum of relative intensities in each rotational or inversion transition is 1. Creswell et al. (1977), Lafferty & Lovas (1978), and Kukolich (1967).

^c (1) and (2) are HEMT amplifier receivers. (3) is an SIS mixer receiver. (4) is a cooled Schottky diode mixer receiver. (5) is a maser receiver.

^d The system temperature was measured in single side band including the atmospheric attenuation.

^e The main beam efficiency.

^f Creswell et al. (1977).

^g The calculated frequency for the main hyperfine components based on the measured frequencies in Alexander et al. (1976).

^h Ho & Townes (1983). The frequency for the main hyperfine components.

serving the SiO maser line ($J = 1 - 0$) from NML Tau, and the averaged pointing accuracy was $\sim 9''$ rms (root mean square of pointing deviations).

2.2. Observations of HC_5N and NH_3

The observations of the ^{13}C isotopic species of HC_5N and NH_3 were carried out toward the cyanopolyne peak in TMC-1 with the Effelsberg 100-m telescope of the Max Planck In-

stitut für Radioastronomie in 1992 April. The ^{13}C isotopic species, $\text{HC}^{13}\text{CCCCN}$ and $\text{HCCCC}^{13}\text{CN}$, were measured using the $J = 9 - 8$ rotational transition at 23.7 GHz region. In addition, the $(J, K) = (2, 2)$ inversion transition of NH_3 was also observed, since this transition fell between the spectral lines of $\text{HC}^{13}\text{CCCCN}$ and $\text{HCCCC}^{13}\text{CN}$, and subsequently, the $(J, K) = (1, 1)$ inversion transition was also observed to derive the rotational temperature (\sim kinetic temperature) and the

Table 2. Spectral line parameters of the ^{13}C isotopic species of HC_3N .

Species & Transition	T_A^* (K)	Δv (km s^{-1})	$\int T_A^* dv$ (K km s^{-1})	rms ^a (mK)	
<i>J</i> = 2 – 1 Cyanopolyne Peak (0', 0')					
HC^{13}CCN	<i>F</i> = 2 – 1	0.022	0.88	0.019	5
	<i>F</i> = 3 – 2	0.042	0.81		
HCC^{13}CN	<i>F</i> = 2 – 1	0.033	0.95	0.033	5
	<i>F</i> = 3 – 2	0.054	0.96		
<i>J</i> = 4 – 3 Cyanopolyne Peak (0', 0')					
H^{13}CCCN	<i>F</i> = 3 – 2	0.084	– ^b	0.19	7
	<i>F</i> = 4 – 3 & 5 – 4	0.19	0.67		
HC^{13}CCN	<i>F</i> = 3 – 2	0.083	– ^b	0.21	12
	<i>F</i> = 4 – 3 & 5 – 4	0.19	0.78		
HCC^{13}CN	<i>F</i> = 3 – 2	0.12	– ^b	0.28	12
	<i>F</i> = 4 – 3 & 5 – 4	0.29	0.71		
<i>J</i> = 5 – 4 Cyanopolyne Peak (0', 0')					
HC^{13}CCN		0.22	0.84	0.20	24
HCC^{13}CN		0.34	0.76	0.27	
NH ₃ Peak (–5', 6')					
HC^{13}CCN		– ^c	– ^c	– ^c	24
HCC^{13}CN		0.12	0.49	0.065	
Southeastern Point (2', –2')					
HC^{13}CCN		0.14	0.67	0.096	24
HCC^{13}CN		0.19	0.59	0.12	

^a The rms noise in emission free region.

^b It is difficult to obtain the line width due to the insufficient separation of the lines.

^c Barely detected

NH₃ column density. As with HC_3N , Table 1 lists the rest frequencies, a receiver, a system noise temperature, a main beam efficiency, and a beam size.

These observations were made in the position switching mode with a reference position of $\Delta \text{R.A.} = -40'$. The intensities of the spectral lines were calibrated by continuum measurements of 3C 123 following the method of Olano et al. (1988). The spectrometer was a 1024 channel autocorrelator used as a single receiver with a bandwidth of 12.5 MHz. The velocity resolution is 0.15 km s^{-1} at 23.7 GHz. The V_{LSR} of TMC-1 was assumed to be 5.85 km s^{-1} . The pointing was checked every two to three hours by observing continuum mainly from 3C 123, and the averaged pointing accuracy was $\sim 6''$ rms (root mean square of pointing deviations).

3. Results and analysis

3.1. Intensity differences among the ^{13}C isotopic species of HC_3N

Spectra of the *J* = 5 – 4 transitions of HC^{13}CCN and HCC^{13}CN measured for the three positions in TMC-1 are shown in Fig. 1.

At each position, the HCC^{13}CN line was observed to have a larger intensity than the HC^{13}CCN line. In particular, the difference in the peak intensities is larger than three times the rms noise (3σ , indicated in the figure) at the cyanopolyne peak. In addition, the HC^{13}CCN line is barely detected at the ammonia peak whereas the HCC^{13}CN line is clearly detected. From these data, the differences in intensities are almost certainly real.

Observed spectra of the *J* = 4 – 3 transitions of H^{13}CCCN , HC^{13}CCN , and HCC^{13}CN at the cyanopolyne peak are shown in Fig. 2a and b. The observed integrated intensity of the HCC^{13}CN line is stronger by a factor of about 1.3 (Sect. 3.2) than that of HC^{13}CCN (in Fig. 2b), and the difference in the peak intensities is significantly larger than three times the rms noise (3σ , indicated in the figure). On the other hand, there is no significant difference in intensities between the H^{13}CCCN and HC^{13}CCN lines. The hyperfine structure due to the electric quadrupole moment of the nitrogen nucleus (nuclear spin of ^{14}N is 1) is partially resolved for each line. The relative intensities and the rest frequencies of the hyperfine components are indicated in the figures.

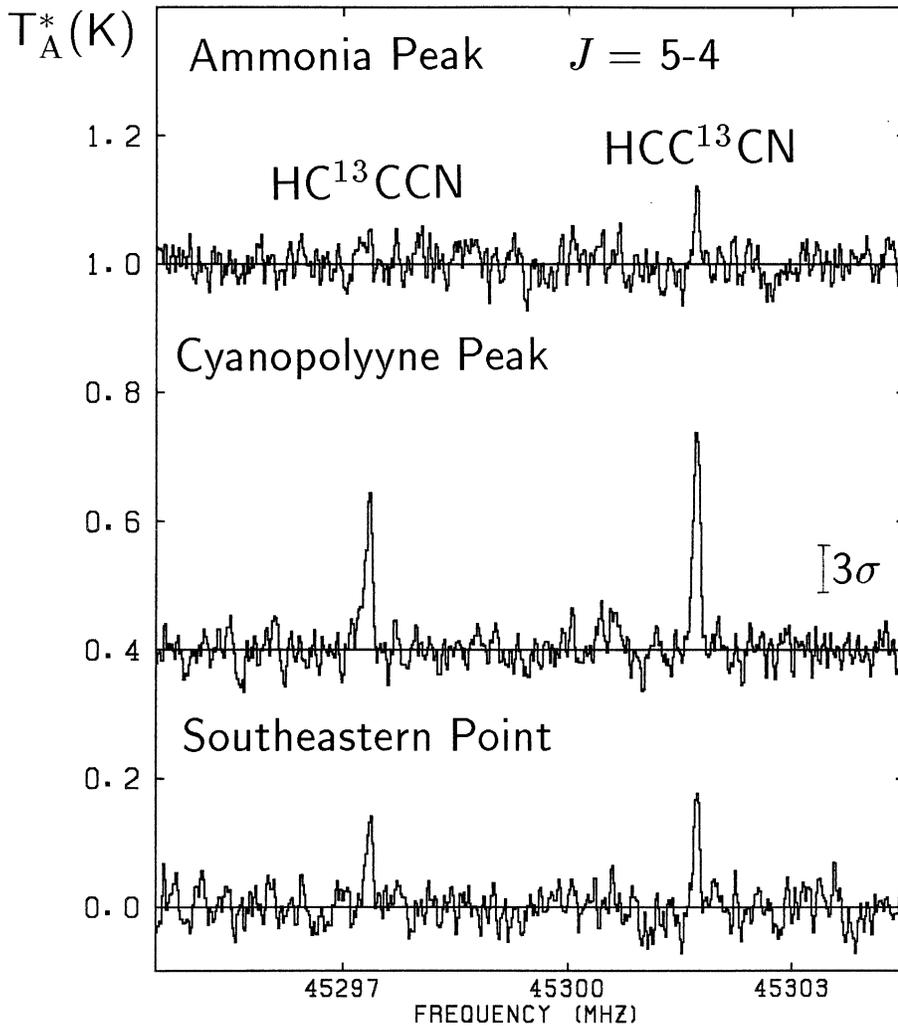


Fig. 1. The $J = 5 - 4$ transitions of HC^{13}CCN and HCC^{13}CN at the three positions in TMC-1 observed with the NRO 45-m telescope: the ammonia peak ($-5', 6'$), the cyanopolyne peak ($0', 0'$), and the southeastern point ($2', -2'$). The ($0', 0'$) position corresponds to (R.A. = $4^{\text{h}}38^{\text{m}}38.8^{\text{s}}$, Decl. = $25^{\circ}35'45''$, epoch 1950.0). The systematic significant differences in intensities are seen at all positions between the lines of HC^{13}CCN and HCC^{13}CN ; the lines of HCC^{13}CN are stronger than those of HC^{13}CCN . Three times of the root mean square (3σ) of the noise in an emission free region is indicated

In addition, the $J = 2 - 1$ transitions of HC^{13}CCN and HCC^{13}CN were observed with partially resolved hyperfine structures at the cyanopolyne peak as shown in Fig. 3. The observed intensity of the HCC^{13}CN line is also stronger than that of the HC^{13}CCN line, though the signal-to-noise ratio is relatively low. Table 2 and 3 list line parameters for the three isotopic species and the normal species, respectively.

Based on these observational results, the intensity differences between ^{13}C isotopomers cannot be due to anomalous excitation or due to accidental overlaps of other spectral lines with the HCC^{13}CN lines, because the differences in intensities between the HC^{13}CCN and HCC^{13}CN lines are found in three transitions. The possibility that the dipole moments of the ^{13}C isotopomers are significantly different each other can be easily excluded, because the differences in intensities are not found in Sgr B2, Ori KL, and IRC+10216. We conclude, therefore, that the differences in intensities are caused by the differences in abundances among the ^{13}C isotopic species, namely, by isotopic fractionation. In addition, the differences in intensities among the ^{13}C isotopic species are detected only in the cold dark cloud TMC-1. This fact also supports that isotopic frac-

tionation, which is enhanced at low temperature, is effective in this case.

3.2. Abundances of the isotopomers of HC_3N

The abundances of the normal and the ^{13}C isotopomers of HC_3N were calculated assuming the local thermodynamic equilibrium (LTE) using the following formula:

$$T_A^* = \eta_B \{ J(T_{\text{ex}}) - J(2.7) \} \{ 1 - \exp(-\tau) \} \quad (2)$$

where

$$J(T) = \frac{h\nu}{k} \left\{ \exp\left(\frac{h\nu}{kT}\right) - 1 \right\}^{-1}, \quad (3)$$

and

$$\tau = \frac{8\pi^3}{3h\Delta\nu} \sqrt{\frac{4\ln 2}{\pi}} \frac{N}{Q} \mu^2 (J_{\text{lower}} + 1) \exp\left\{-\frac{E_{\text{lower}}}{kT_{\text{ex}}}\right\} \times \left\{ 1 - \exp\left(-\frac{h\nu}{kT_{\text{ex}}}\right) \right\} S \text{ (relative)}. \quad (4)$$

In these formulae, T_A^* denotes the antenna temperature, η_B is the main beam efficiency, T_{ex} is the excitation temperature, τ

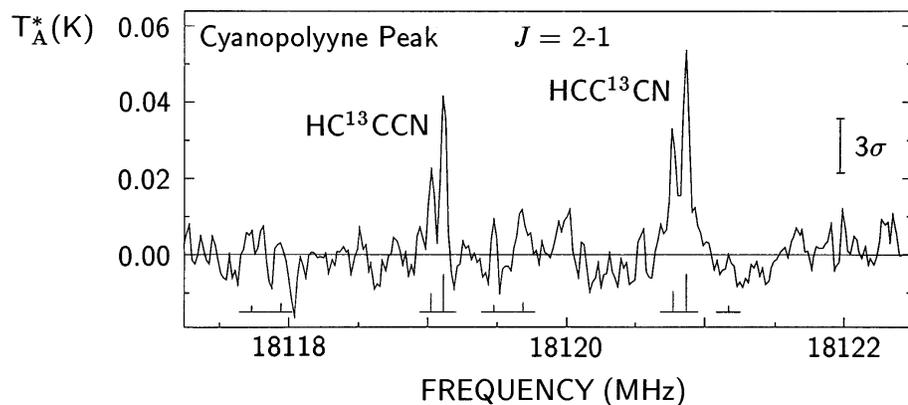
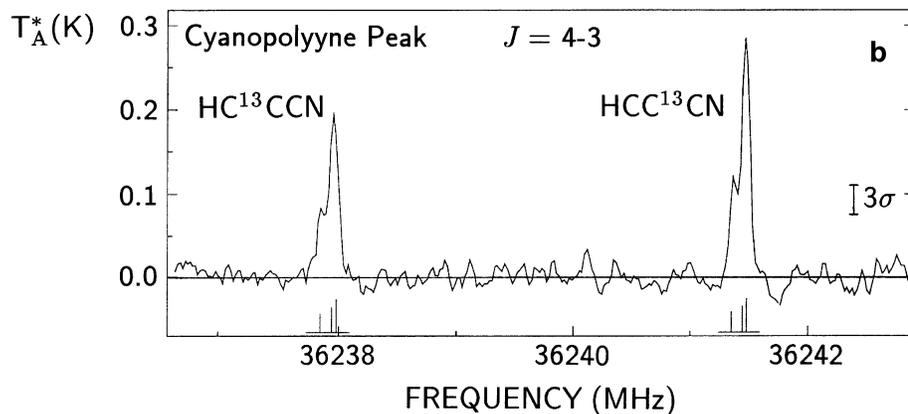
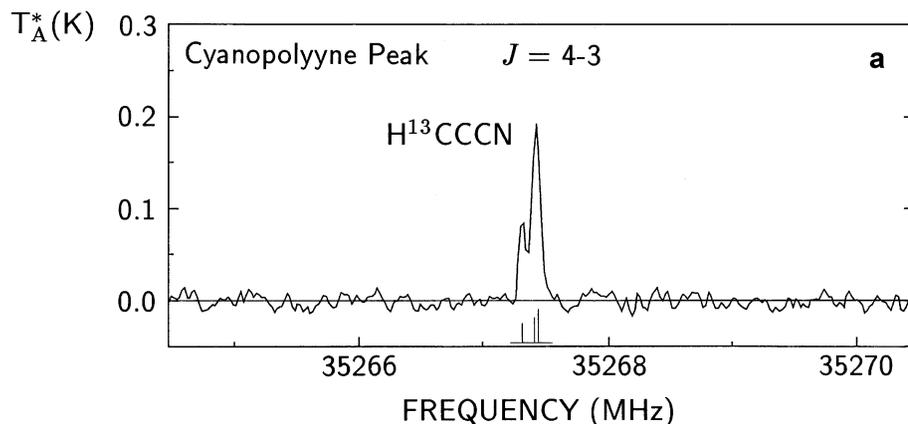


Fig. 2a and b. The $J = 4 - 3$ transitions of H^{13}CCCN **a**, HC^{13}CCN and HCC^{13}CN **b** at the cyanopolyne peak in TMC-1 observed with the NRO 45-m telescope. The intensity of the HCC^{13}CN line is definitely stronger than that of HC^{13}CCN . On the other hand, no significant difference is found between the intensities of the H^{13}CCCN and HC^{13}CCN lines. The hyperfine splitting due to the nuclear quadrupole interaction of the nitrogen nucleus is partially resolved for each rotational line. The positions of the hyperfine components are indicated based on the laboratory frequencies with the theoretical relative intensities. In **b** three times of the root mean square (3σ) of the noise in an emission free region is indicated

Fig. 3. The $J = 2 - 1$ transitions of HC^{13}CCN and HCC^{13}CN at the cyanopolyne peak in TMC-1 observed with the NRO 45-m telescope. The intensity of the HCC^{13}CN line is stronger than that of HC^{13}CCN . The hyperfine splitting due to the nuclear quadrupole interaction of the nitrogen nucleus is partially resolved for each rotational line. The positions of the hyperfine components are indicated based on the laboratory frequencies with the theoretical relative intensities. Three times of the root mean square (3σ) of the noise in an emission free region is indicated

is the optical depth, $\Delta\nu$ is the line width (FWHP), N is the column density, Q is the partition function neglecting hyperfine structure, μ is the permanent electric dipole moment (3.729 debye for HC_3N ; Kasten & Dreizler, 1984), E_{lower} is the energy level of the lower state of the transition, and $S(\text{relative})$ is the relative intensity of each hyperfine component (The sum for each rotational transition is 1).

The rotational temperature and the column density of normal HC_3N at the cyanopolyne peak were determined to be (7.1 ± 0.1) K and $(1.6 \pm 0.1) \times 10^{14} \text{ cm}^{-2}$, where the errors correspond to one standard deviation. In this calculation, the observed intensities of the $J = 2 - 1$, $4 - 3$, $5 - 4$, and $10 - 9$

transitions were analyzed by least-squares method. The beam filling factors are assumed to be 1 for all calculations in this section. The partially overlapped hyperfine components were not included in the analysis. Suzuki et al. (1992) reported the column density of HC_3N to be $1.71 \times 10^{14} \text{ cm}^{-2}$ using the $J = 5 - 4$ transition with the NRO 45-m telescope, if the excitation temperature is 6.5 K. Our column density is in good agreement with their result. At the ammonia peak, the rotational temperature and the column density were obtained to be 5.5 K and $3.6 \times 10^{13} \text{ cm}^{-2}$ using the observed intensities of the $J = 5 - 4$ and $10 - 9$ transitions. At the southeastern position, the rotational temperature and the column density were obtained to be

Table 3. Spectral line parameters of the normal species of HC_3N .

Transition	T_A^* (K)	Δv (km s^{-1})	rms ^a (mK)
<i>J</i> = 2 – 1 Cyanopolyne Peak ($0', 0'$)			
<i>F</i> = 2 – 2	0.49	0.91	6
1 – 0	0.58	0.91	
2 – 1	1.1	0.98	
3 – 2	1.7	0.94	
1 – 2	0.045	1.07	
1 – 1	0.49	0.89	
<i>J</i> = 4 – 3 Cyanopolyne Peak ($0', 0'$)			
<i>F</i> = 4 – 4	0.62	0.57	33
3 – 2	2.8	– ^b	
4 – 3			
& 5 – 4	3.5	– ^b	
3 – 3	0.59	0.59	
<i>J</i> = 5 – 4 Cyanopolyne Peak ($0', 0'$)			
<i>F</i> = 4 – 4	0.39	0.52	27
4 – 3, 5 – 4			
& 6 – 5	2.9	1.00	
5 – 5	0.38	0.52	
NH ₃ Peak ($-5', 6'$)			
<i>F</i> = 4 – 4	– ^c	– ^c	26
4 – 3, 5 – 4			
& 6 – 5	1.5	0.87	
5 – 5	– ^c	– ^c	
Southeastern Point ($2', -2'$)			
<i>F</i> = 4 – 4	0.17	0.42	24
4 – 3, 5 – 4			
& 6 – 5	2.0	0.90	
5 – 5	0.20	0.41	
<i>J</i> = 10 – 9 Cyanopolyne Peak ($0', 0'$)			
	2.0	0.49	76
NH ₃ Peak ($-5', 6'$)			
	0.82	0.38	72
Southeastern Point ($2', -2'$)			
	0.87	0.49	104

^a The rms noise in emission free region.

^b The lines are not well resolved.

^c Not detected.

5.9 K and $6.7 \times 10^{13} \text{ cm}^{-2}$. In this calculation, the observed intensities of the hyperfine components of the *J* = 5 – 4 transition were analyzed by least-squares method. The errors (1σ) for the column densities in the ammonia peak and the southeastern point were estimated to be 10% (similar to that in the cyanopolyne peak).

The abundances of the ^{13}C isotopomers were calculated using the integrated intensities with the excitation temperatures of the normal species at the corresponding positions assuming optically thin limit. The column densities obtained are listed in Table 4. The ratios of the column densities of the three ^{13}C isotopic species (at the cyanopolyne peak) are $1.4(\pm 0.2)$ for $[\text{HCC}^{13}\text{CN}]/[\text{HC}^{13}\text{CCN}]$

Table 4. Column densities of the normal and ^{13}C isotopic species of HC_3N , and the carbon isotopic ratios (column density ratios).

Species	Column Density ^a (cm^{-2})	Carbon Isotopic Ratio ^b [Normal Species] / [^{13}C Species]
Ammonia Peak ($-5', 6'$)		
HC_3N	$(3.6 \pm 0.4) \times 10^{13}$	–
HCC^{13}CN	$(8.0 \pm 0.8) \times 10^{11}$	45 ± 6
Cyanopolyne Peak ($0', 0'$)		
HC_3N	$(1.6 \pm 0.1) \times 10^{14}$	–
H^{13}CCCN	$(2.0 \pm 0.2) \times 10^{12}$	79 ± 11
HC^{13}CCN	$(2.1 \pm 0.2) \times 10^{12}$	75 ± 10
HCC^{13}CN	$(2.9 \pm 0.3) \times 10^{12}$	55 ± 7
Southeastern Point ($2', -2'$)		
HC_3N	$(6.7 \pm 0.7) \times 10^{13}$	–
HC^{13}CCN	$(1.1 \pm 0.1) \times 10^{12}$	61 ± 9
HCC^{13}CN	$(1.3 \pm 0.1) \times 10^{12}$	50 ± 7

^a In case of the normal species of HC_3N at the cyanopolyne peak, the error for the column density corresponds to one standard deviation obtained by least-squares analysis. In other cases, the errors (1σ) for the column densities are estimated to be 10% of them.

^b The errors correspond to one standard deviation. The errors are probably overestimated (see Sect. 3.2 and 3.3).

and

$$0.95(\pm 0.13) \text{ for } [\text{H}^{13}\text{CCCN}]/[\text{HC}^{13}\text{CCN}],$$

where the errors (1σ) are calculated from those of column densities (10% uncertainty was estimated as 1σ) listed in Table 4. However, the errors for the column densities of the three ^{13}C isotopic species should correlate each other, because each observation as follows was carried out simultaneously: HC^{13}CCN and HCC^{13}CN (*J* = 2 – 1); H^{13}CCCN , HC^{13}CCN , and HCC^{13}CN (*J* = 4 – 3); HC^{13}CCN and HCC^{13}CN (*J* = 5 – 4). Since the effect of the correlations is not taken into account, the errors for the column density ratios shown above are probably overestimated. The ratios of the integrated intensities of the *J* = 4 – 3 transitions are

$$1.33 \pm 0.08 \text{ for } \text{HCC}^{13}\text{CN}/\text{HC}^{13}\text{CCN}$$

and

$$0.90 \pm 0.05 \text{ for } \text{H}^{13}\text{CCCN}/\text{HC}^{13}\text{CCN},$$

where the errors (1σ) are calculated from the rms noise in the spectra.

3.3. The carbon isotopic ratios

The carbon isotopic ratios ($^{12}\text{C}/^{13}\text{C}$) were calculated from the obtained column densities of the normal and isotopic species of HC_3N , and the ratios are also listed in Table 4. The isotopic ratios reflect the differences in the abundances of the three ^{13}C isotopic species. The carbon isotopic ratios obtained from H^{13}CCCN and HC^{13}CCN (79 ± 11 and 75 ± 10) at the cyanopolyne peak do not significantly deviate from the solar value of 89 or from the value of ~ 70 in the solar neighborhood (see Wilson & Rood 1994), but the ratios obtained from

Table 5. Spectral line parameters of the ^{13}C isotopic species of HC_5N

Species & Transition	T_B (K)	Δv (km s^{-1})	$\int T_B dv$ (K km s^{-1})	rms ^a (mK)
Cyanopolyne Peak ($0', 0'$)				
$J = 9 - 8$ HC 13 CCCCN	0.11	0.51	0.057	13.5
HCCCC 13 CN	0.12	0.54	0.073	

^a The rms noise in emission free region.

HCC 13 CN at all three positions (45 ~ 55) are significantly lower than those obtained from H 13 CCCN and HC 13 CCN. Therefore, we conclude that the ^{13}C isotope is concentrated in a carbon atom adjacent to the nitrogen atom in HC_3N . The errors for the isotopic ratios are probably overestimated due to the same reason for the column density ratios in the preceding section.

3.4. Intensity difference among the ^{13}C isotopic species of HC_5N

The spectral line parameters of the $J = 9 - 8$ rotational transitions of the ^{13}C isotopic species of HC_5N (HC 13 CCCCN and HCCCC 13 CN) at the cyanopolyne peak are listed in Table 5, and the spectra are shown in Fig. 4. The intensity of the HCCCC 13 CN line is slightly larger than that of the HC 13 CCCCN line. The integrated intensity ratio of the two ^{13}C isotopic species (HCCCC 13 CN/HC 13 CCCCN) is determined to be 1.29 ± 0.15 , where the error was calculated from the rms noise in the spectra and corresponds to one standard deviation. The tendency that the ^{13}C isotope seems to be concentrated in a carbon atom adjacent to the nitrogen atom in HC_5N is the same as in the case of HC_3N . However the data for the ^{13}C isotopomers of HC_5N are limited to two species in the $J = 9 - 8$ transition. We conclude, therefore, that isotopic fractionation in HC_5N is not definite, but probable.

3.5. Analysis of NH_3 data

The line parameters are listed in Table 6 for the NH_3 (J, K) = (1, 1) and (2, 2) emission, and the spectra are shown in Fig. 5 and Fig. 4, respectively. We analyzed the NH_3 data using the method of Ho et al. (1979) and Ungerechts et al. (1980). First, the optical depth of the main hyperfine component of the (1, 1) transition was calculated using the relative intensities of the hyperfine components (Kukolich 1967), and the derived value is 0.99 ± 0.43 , where all of errors in this section correspond to one standard deviation. Then, assuming a beam filling factor of unity, the excitation temperature of the (1, 1) inversion doublet was calculated to be $6.5_{-0.6}^{+1.8}$ K. Our value for the rotational temperature between the (1, 1) and (2, 2) levels ($\sim T_K$) is 9.4 ± 0.8 K, which is close to the kinetic temperatures ($9.3 \sim 11.2$ K) obtained in the northern ridge of TMC-1 (Gaida et al. 1984). Finally, we find that the column density of para- NH_3 ((1, 1) and (2, 2) doublets) is $(1.3 \pm 0.6) \times 10^{14} \text{ cm}^{-2}$. This value is in good agreement with the column density of the (1, 1) doublet, $1 \times 10^{14} \text{ cm}^{-2}$, estimated by Gaida et al. (1984) from observations

Table 6. Spectral line parameters of NH_3

Transition	T_B (K)	Δv (km s^{-1})	$\int T_B dv$ (K km s^{-1})	rms ^a (mK)
Cyanopolyne Peak ($0', 0'$)				
(J, K) = (1, 1)				60
$F_1 = 0 - 1$	0.70	0.70	0.38	
2 - 1	0.82	0.70	0.56	
1 - 1 & 2 - 2	2.4	0.72	1.7	
1 - 2	0.87	0.89	0.61	
1 - 0	0.93	0.53	0.45	
(J, K) = (2, 2)	0.16	0.48	0.068	13.5

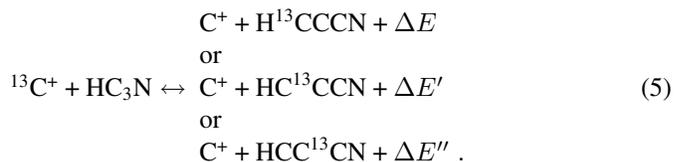
^a The rms noise in emission free region.

with the Effelsberg 100-m telescope. Assuming LTE, the total (ortho and para) column density of NH_3 is $(2.6 \pm 1.2) \times 10^{14}$ or $(6.5 \pm 3.0) \times 10^{14} \text{ cm}^{-2}$, for an ortho/para ratio of 1 (high-temperature limit) or 4 (~ 10 K), respectively. Suzuki et al. (1992) reported the column density of NH_3 as $1.9 \times 10^{14} \text{ cm}^{-2}$, which is slightly lower than our values.

4. Discussion

4.1. The mechanism for ^{13}C isotopic fractionation in HC_3N

Generally, isotopic fractionation is thought to occur by isotope exchange reactions as mentioned in the introduction. First, we examined whether ^{13}C isotopic fractionation among the three carbon sites in HC_3N could be caused by the following isotope exchange reaction after the HC_3N formation (and before the HC_3N destruction):



This isotope exchange reaction can be excluded as a main process for following two reasons.

(1) We calculated the heats of reactions (ΔE , $\Delta E'$, and $\Delta E''$) to estimate the branching ratios of the reaction (5) based on the internuclear distances and the force constants of HC_3N (Wolfsberg et al. 1979). The heats of reactions obtained are $\Delta E = 48.9$, $\Delta E' = 56.8$, and $\Delta E'' = 63.8$ K. The result is also shown schematically in Fig. 6. A part of this result was also calculated by Wolfsberg et al. (1979). From Fig. 6, the difference in the zero-point energies between HC_3N and H 13 CCCN is 48.9 K ($= \Delta E$), which is much larger than those among the three ^{13}C isotopic species (7.9 K and 7.1 K). This means that the ^{13}C isotope must be concentrated in H 13 CCCN, HC 13 CCN, and HCC 13 CN to almost the same degree at low temperatures, so that all of the carbon isotopic ratios ($[\text{HC}_3\text{N}]/[\text{H}^{13}\text{CCCN}]$, $[\text{HC}_3\text{N}]/[\text{HC}^{13}\text{CCN}]$, and $[\text{HC}_3\text{N}]/[\text{HCC}^{13}\text{CN}]$) should be similar, and much lower than the solar value or interstellar value in

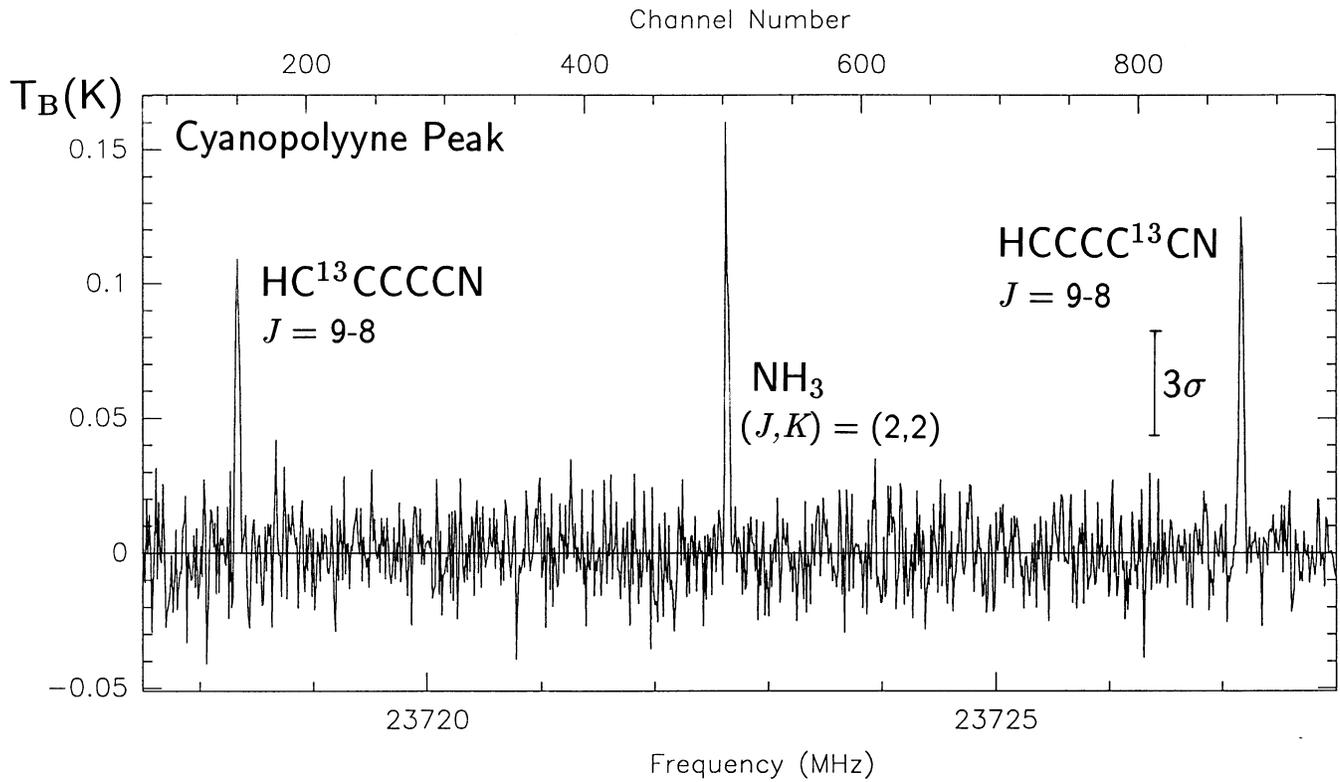


Fig. 4. The $J = 9 - 8$ transitions of $\text{HC}^{13}\text{CCCCN}$ and $\text{HCCCC}^{13}\text{CN}$, and the $(J, K) = (2, 2)$ inversion transition of NH_3 at the cyanopolyne peak in TMC-1 observed with the Effelsberg 100-m telescope. Three times of the root mean square (3σ) of the noise in an emission free region is indicated

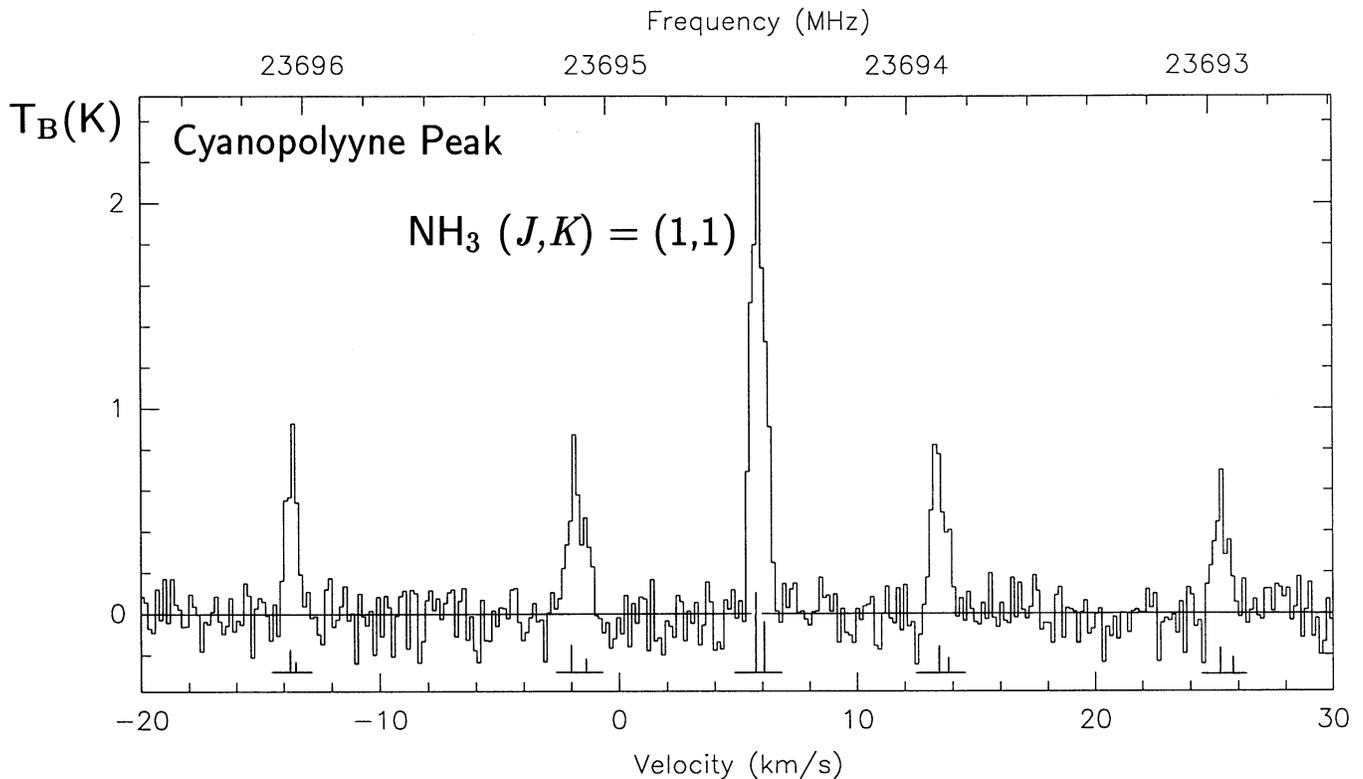


Fig. 5. The $(J, K) = (1, 1)$ inversion transition of NH_3 at the cyanopolyne peak in TMC-1 observed with the Effelsberg 100-m telescope. The velocity scale is for the central hyperfine component. The positions and the relative intensities of the strong hyperfine components are indicated (Kukolich 1967; Rydbeck et al. 1977)

the solar neighborhood. However, this expectation contradicts the observational results.

(2) Laboratory measurements of the ion-molecule reaction between C^+ and HC_3N show that the products are C_3H^+ (80%) and C_4N^+ (20%) (Raksit & Bohme 1985), and C_3H^+ (65%) and C_4N^+ (28%) (Knight et al. 1986). They compared their reactive rate coefficients with theoretical collisional rate coefficients, and found that the two corresponding values are close to each other. Therefore, the main products of the reaction (5) should not be ^{13}C substituted HC_3N , but the ^{13}C substituted C_3H^+ and C_4N^+ .

We conclude, therefore, that ^{13}C isotopic fractionation must occur in the formation process of HC_3N , not after the formation of HC_3N . The present consideration may be generalized to the cases of other longer cyanopolyynes.

We now review proposed formation processes of HC_3N in dark clouds and discuss the probable processes which can explain ^{13}C isotopic fractionation. The formation of HC_3N is a matter of some controversy (e.g. Knight et al. 1986; Winnewisser & Herbst 1987). In ion-molecule reactions, HC_3N is produced by an electron recombination of HC_3NH^+ as follows:

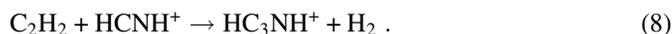


The first possible mechanism to produce HC_3NH^+ is (Schiff & Bohme 1979, Huntress 1977),



(e.g. $k_7 = 5.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 305 K, Knight et al. 1986; $3.78 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K, Iraqi et al. 1990).

The second is (Mitchell et al. 1979),



The third is (Herbst 1983, Herbst et al. 1984),



($k_9 = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Federer et al. 1986).

The fourth is via HC_3N^+ as follows (Leung et al. 1984; Herbst et al. 1984; Winnewisser & Herbst 1987):



then,



($k_{12} = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K, Knight et al. 1985; $9.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K, Fox et al. 1986). Freeman & Millar (1983) also proposed that ion-molecule reactions between hydrocarbons and atomic nitrogen are generally important for the production of cyanopolyynes. The reactions (7), (9), and (12) have been studied in laboratory as indicated. Based on these results, Knight et al. (1986) concluded that the reaction (9) is the most probable route for the formation of HC_3N .

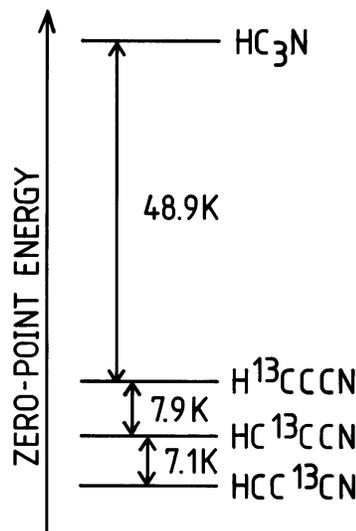


Fig. 6. A schematic of the differences in the zero-point energies is shown for HC_3N and the three ^{13}C isotopic species of HC_3N

Then, a following neutral-neutral reaction has been proposed (Herbst & Leung 1990):



Sims et al. (1993) reported that the rate coefficients of the reaction between C_2H_2 and CN are fast ($4.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) down to 25 K. Liao & Herbst (1995) tried to explain these experimental rate coefficients using long-range capture theories. Although they could not reproduce the experimentally measured temperature dependence, their calculated rate coefficients are in reasonable agreement with the measured coefficients at low temperatures. In addition, an ab initio calculation of this neutral-neutral reaction by Woon & Herbst (1996, 1997) showed that there are no significantly high energy barriers to hinder the reaction, and they succeeded in reproducing the temperature dependence of the rate coefficient, between 10 and 300 K. Fukuzawa & Osamura (1996) also studied this reaction by ab initio calculation, and they found no significantly high energy barriers to hinder the reaction. These calculations support the relatively large rate coefficient of this reaction at low temperatures. The possibility of this neutral-neutral reaction is also supported by a detection of a metastable isomer HNC_3 in TMC-1 (Kawaguchi et al. 1992), where HNC_3 and HC_3N are produced from the same precursor ion HC_3NH^+ in ion-molecule reaction scheme, but the observed abundance of HNC_3 was only $1/160 \sim 1/450$ of that of HC_3N .

The following neutral-neutral reaction was also found to have no significant energy barriers by ab initio calculations (Fukuzawa & Osamura 1996):



This reaction may also contribute to the formation of HC_3N .

Next, we discuss whether each of the reactions above can explain the observed ^{13}C isotopic fractionation in HC_3N . Concerning the third mechanism (reaction (9)), the C_3H_3^+ ion is known to have two isomers: the cyclic form (*c*- C_3H_3^+) with D_{3h} symmetry and the linear form (*l*- C_3H_3^+) with C_{2v} symmetry. The cyclic form is more stable than the linear form based on ab initio calculations ($7.43 \sim 8.46 \text{ kJ mol}^{-1}$, Raghavachari et al. 1981) and on an experiment (5.7 kJ mol^{-1} , Rosenstock et al. 1977). Since *c*- C_3H_3^+ ion has three equivalent carbons, this ion cannot contribute to ^{13}C isotopic fractionation among the three carbon sites in HC_3N .

In addition, the contribution of the fourth mechanism (reactions (10)–(12)) to ^{13}C isotopic fractionation seems quite small, because following two conditions are necessary for the contribution:

(1) the ^{13}C isotope should be concentrated in one specific carbon atom in C_3H_2^+ and/or C_3H_2 , and

(2) in the reactions (10) and (11), nitrogen atom should always make a bond with a carbon concentrated in ^{13}C .

Both conditions seem difficult to realize. Concerning the condition (1), the *c*- C_3H_2 and *l*- C_3H_2 molecules are already detected in interstellar space (Vrtilek et al. 1987; Cernicharo et al. 1991), but there is no detailed information on the abundances of the ^{13}C isotopic species in TMC-1. We conclude that the third (reaction(9)) and fourth (reactions (10)–(12)) mechanisms cannot completely dominate for the formation of HC_3N .

The observational result of the enhanced abundance of the ^{13}C isotope in the CN group can be explained if HC_3N is produced via reactions (7), (8), (13), and/or (14), subject to the following two conditions:

(1) the ^{13}C isotope is concentrated in the precursors of HC_3N such as HCN, HCNH^+ , CN, and/or HNC, but not significantly in C_2H_2^+ , C_2H_2 , and/or C_2H , and

(2) the CN bond in HCN, HCNH^+ , CN, and/or HNC must be preserved when HC_3N is produced.

To check the validity of the condition (1), observational studies of the carbon isotopic ratios for the precursors of HC_3N in TMC-1 are useful. On the other hand, the carbon isotope ratios in diffuse clouds toward ζ Oph obtained from CN are $47.3^{+5.5}_{-4.4}$ (Crane & Hegyi 1988), 100^{+88}_{-33} (Hawkins et al. 1993), and 35 ± 13 (Roth & Meyer 1995). If the lower values are correct, the ^{13}C isotope may already be concentrated in CN in diffuse clouds toward ζ Oph. If so, these facts may support condition (1), because fractionation is easier in dark clouds than in diffuse clouds due to lower temperatures in dark clouds. Concerning condition (2), it is interesting that Creswell et al. (1977) found experimentally that the rotational spectrum of HCC^{13}CN was much more intense than that of HC^{13}CCN , when the ^{13}C enriched HC_3N were produced in discharge in a mixture of C_2H_2 and H^{13}CN . This fact suggests that the CN triple bond is strong enough to survive from H^{13}CN to HCC^{13}CN in their experimental set up. This result may support the condition (2) that the CN group in interstellar HC_3N arises from HCN, HCNH^+ , CN, and/or HNC.

4.2. Possible mechanisms of the concentration and the non-concentration of the ^{13}C isotope in the precursor molecules for HC_3N

We briefly discuss possible mechanisms of the concentration and the non-concentration of the ^{13}C isotope in the precursor molecules of HC_3N , namely, the molecules with a CN group (HCN, HCNH^+ , CN, and HNC) and the hydrocarbons (C_2H_2^+ , C_2H_2 , C_3H_3^+ , C_3H_2^+ , C_3H_2 , and C_2H). Here we will restrict ourselves to the discussion mainly in the aspect of isotope exchange reactions after these molecules are formed, although their carbon isotopic ratios may also change in the formation processes of them. However, it is difficult to discuss these formation processes reliably, because the formation processes of them and related possible isotope exchange reactions are not well understood.

For HCN, HCNH^+ , CN, and HNC, probable isotope exchange reactions are as follows:



The reaction between C^+ and HCN has already been studied in laboratory (e.g. Anicich et al. 1986; Clary et al. 1990). Since they reported that the product ion is only C_2N^+ ($k = 2.9 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K, Clary et al. 1990) and that C_2N^+ is produced near the capture rate, the reaction (15) does not realize. No laboratory data are reported for the reactions (16)–(18), but the value of ΔE is estimated to be 34 K for the reaction (17) (Kaiser et al. 1991; Langer 1992).

It is reasonable to assume that many kinds of reaction products appear as the number of atoms in a reactant molecule increases. Therefore, a carbon isotope exchange reaction seems to be dominant only when the number of atoms in a reactant molecule is small and probably when there is a carbon atom at the terminal position in the reactant molecule. With this viewpoint the reaction (17) is the most probable reaction to introduce concentrated ^{13}C isotope in the CN group, though the reactions (16) and (18) cannot be excluded in the present stage.

The isotope exchange reactions are not well studied for the hydrocarbons either. Only the reaction between C^+ and C_2H_2 is studied in laboratory (e.g. Anicich et al. 1986). They reported that the main products of this reaction are only C_3H^+ and H as follows:



($k_{19} = 2.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, Anicich et al. 1986). The value of k_{19} seems to be close to the collision rate coefficient, though no calculated coefficient has been reported. Therefore, a concentration of the ^{13}C isotope in C_2H_2 by the isotope exchange reaction probably does not occur. Since other hydrocarbons have similar or larger size than C_2H_2 , isotope exchange reactions for them are difficult to realize either. The ^{13}C

isotope is, therefore, probably not enriched in these hydrocarbons at least after they are formed.

In addition, if the ^{13}C isotope is not concentrated in interstellar C^+ , and if the interstellar hydrocarbons react with C^+ efficiently as in the case of the reaction (19), it is possible to assume that carbon atoms are circulating between C^+ and the hydrocarbons relatively rapidly and that the carbon isotopic ratios of them may approach to that of C^+ .

The results of these discussions do not contradict the condition (1) for reactions (7), (8), (13), and/or (14) mentioned in the last paragraph of Sect. 4.1. However, formation processes of the precursor molecules should be studied in detail in the future to obtain more definite conclusions.

Recently Kaiser et al. (1997) reported experimental studies of several reactions between neutral carbon atoms and neutral unsaturated hydrocarbons. Their experiments were carried out at relative collision energies between 8.8 and 45 kJ mol^{-1} , which are much higher than kinetic temperatures in dark clouds including TMC-1. However, if such reactions are rapid in dark clouds, formation mechanisms of carbon containing molecules as well as carbon isotope exchange reactions should be reconsidered. Additional low-temperature experiments are necessary to know whether these neutral atom - neutral molecule reactions are important in dark clouds.

4.3. The ratio of the contributions of two types of formation reactions which do and do not produce ^{13}C isotopic fractionation

Based on the probable mechanisms of ^{13}C isotopic fractionation discussed in the former sections and on their reaction rate coefficients, the most important formation reaction of HC_3N is probably the reaction between C_2H_2 and CN (reaction(13)). However, other reactions may also contribute to the HC_3N formation. We discuss the ratio of the contributions of two types of reactions which produce ^{13}C isotopic fractionation (reactions (7), (8), (13), and (14)) and which do not produce ^{13}C isotopic fractionation (reactions (9), (10), and (11)).

We assume that the precursor molecules of HC_3N have same carbon isotopic ratio ([normal species]/[^{13}C mono-substituted species]) if their number of carbon atom is the same. We define ratios as follows:

$$\begin{aligned} [\text{HCN}]/[\text{H}^{13}\text{CN}] &= [\text{HCNH}^+]/[\text{H}^{13}\text{CNH}^+] \\ &= [\text{CN}]/[\text{C}^{13}\text{N}] = [\text{HNC}]/[\text{HN}^{13}\text{C}] = r_1, \end{aligned} \quad (20)$$

$$\begin{aligned} [\text{CCH}]/[\text{C}^{13}\text{CCH}] &= [\text{CCH}]/[\text{C}^{13}\text{CH}] \\ &= 2 \times [\text{HC}_2\text{H}^+]/[\text{HC}^{13}\text{CH}^+] = 2 \times [\text{HC}_2\text{H}]/[\text{HC}^{13}\text{CH}] = r_2, \end{aligned} \quad (21)$$

and

$$\begin{aligned} [1 - \text{C}_3\text{H}_2^+]/[1 - \text{C}_3\text{H}_2^+] &= [1 - \text{C}_3\text{H}_2]/[1 - \text{C}_3\text{H}_2] \\ &= [\text{c} - \text{C}_3\text{H}_2^+]/[\text{c} - \text{C}_3\text{H}_2^+] \quad ({}^{13}\text{C} \text{ in the } \text{C}_{2v} \text{ axis}) \\ &= [\text{c} - \text{C}_3\text{H}_2]/[\text{c} - \text{C}_3\text{H}_2] \quad ({}^{13}\text{C} \text{ in the } \text{C}_{2v} \text{ axis}) \\ &= 2 \times [\text{c} - \text{C}_3\text{H}_2^+]/[\text{c} - \text{C}_3\text{H}_2^+] \quad ({}^{13}\text{C} \text{ not in the } \text{C}_{2v} \text{ axis}) \end{aligned}$$

$$\begin{aligned} &= 2 \times [\text{c} - \text{C}_3\text{H}_2]/[\text{c} - \text{C}_3\text{H}_2] \quad ({}^{13}\text{C} \text{ not in the } \text{C}_{2v} \text{ axis}) \\ &= 3 \times [\text{c} - \text{C}_3\text{H}_3^+]/[\text{c} - \text{C}_3\text{H}_3^+] = r_3. \end{aligned} \quad (22)$$

In addition, “ R ” is defined as an average isotopic ratio of the entire carbon in the source. (If we assume that there is no isotopic fractionation at all, a relation $R = r_1 = r_2 = r_3$ holds.)

First, we consider reactions which produce isotopic fractionation. Then, in this case, the abundance ratios of the ^{13}C isotopic species of HC_3N are expressed as follows:

$$\begin{aligned} [\text{H}^{13}\text{CCCN}] : [\text{HC}^{13}\text{CCN}] : [\text{HCC}^{13}\text{CN}] : [\text{HC}_3\text{N}] \\ = 1 : 1 : r_2/r_1 : r_2. \end{aligned} \quad (23)$$

Second, the reactions which do not produce isotopic fractionation are considered, where molecules containing three carbon atoms and nitrogen atom react. In this case, the abundance ratios of the isotopic species are as follows:

$$\begin{aligned} [\text{H}^{13}\text{CCCN}] : [\text{HC}^{13}\text{CCN}] : [\text{HCC}^{13}\text{CN}] : [\text{HC}_3\text{N}] \\ = 1 : 1 : 1 : r_3. \end{aligned} \quad (24)$$

We define the ratio of the contributions of the first and the second type of reactions to be $y : 1 - y$ ($0 \leq y \leq 1$), and we also define the column density of H^{13}CCCN to be “ N ”. Then the column densities of the isotopomers and the normal species, as a result of two types of reactions, are expressed as follows:

$$[\text{H}^{13}\text{CCCN}] \{ = Ny + N(1 - y) \} = N, \quad (25)$$

$$[\text{HC}^{13}\text{CCN}] \{ = Ny + N(1 - y) \} = N, \quad (26)$$

$$[\text{HCC}^{13}\text{CN}] = Ny r_2/r_1 + N(1 - y), \quad (27)$$

$$[\text{HC}_3\text{N}] = Ny r_2 + N(1 - y) r_3. \quad (28)$$

Then the abundance ratios are expressed as follows:

$$\begin{aligned} [\text{HC}_3\text{N}]/[\text{H}^{13}\text{CCCN}] \\ = [\text{HC}_3\text{N}]/[\text{HC}^{13}\text{CCN}] = y r_2 + (1 - y) r_3, \end{aligned} \quad (29)$$

$$\begin{aligned} [\text{HC}_3\text{N}]/[\text{HCC}^{13}\text{CN}] \\ = \{ y r_2 + (1 - y) r_3 \} / \{ y r_2/r_1 + (1 - y) \}, \end{aligned} \quad (30)$$

$$\begin{aligned} [\text{HCC}^{13}\text{CN}]/[\text{H}^{13}\text{CCCN}] \\ = [\text{HCC}^{13}\text{CN}]/[\text{HC}^{13}\text{CCN}] = y r_2/r_1 + (1 - y). \end{aligned} \quad (31)$$

The last formula has a value of 1.4 (Sect. 3.2), and it shows the relation between r_2/r_1 and y as follows:

$$y r_2/r_1 + (1 - y) = 1.4, \quad (32)$$

then,

$$r_2/r_1 = 1 + 0.4/y \geq 1.4. \quad (33)$$

The minimum value of r_2/r_1 becomes 1.4 when $y = 1$. This minimum value indicates that the value of r_1 should be as follows if we assume no isotopic fractionation for r_2 (in this case $r_2 = R$):

$$r_1 \leq r_2/1.4 = 0.71 R. \quad (34)$$

This result indicates that more than 30% of ^{13}C isotopic fractionation is necessary for HCN , HCNH^+ , CN , and/or HNC to explain the present observational results.

The value of y can be calculated using the formula (33) by assuming various values of r_1 . In this case, the value of r_2 in the formula (33) is fixed to 77, which is the average value of the carbon isotopic ratios obtained by H^{13}CCCN and HC^{13}CCN (Table 4), assuming $r_2 = r_3$ in the formula (29). When the assumed value of r_1 is between 55 and 43, the formation reactions which produce ^{13}C isotopic fractionation are main ($y > 0.5$). However, when the assumed value of r_1 is extremely low (< 43), the formation reactions which do not produce ^{13}C isotopic fractionation become main ($y < 0.5$).

Although such a high fractionation ($^{12}\text{C}/^{13}\text{C} < 43$) does not seem to be plausible, actual measurements of ^{13}C isotopic fractionation in HCN , HCNH^+ , CN , and HNC are important to check the formula (34), to select which of the contributions are important for the origin of the ^{13}C isotope in HCC^{13}CN .

4.4. ^{13}C isotopic fractionation in HC_5N

Although the observed ^{13}C isotopic species are limited to $\text{HC}^{13}\text{CCCCN}$ and $\text{HCCCC}^{13}\text{CN}$, a probable difference in intensities was found as mentioned in Sect. 3.4. This result supports the idea that part of formation mechanisms are the same for HC_3N and HC_5N . Our reasoning is as follows:

(1) the ^{13}C enriched CN group is preserved from HC_3N to HC_5N if the CN group is connected to the carbon chain part in the initial stage of the carbon chain growth, or

(2) the ^{13}C enriched CN containing species are connected to the carbon chains to produce HC_3N and HC_5N after the carbon chains for HC_3N and HC_5N are separately formed.

Recently, Fukuzawa & Osamura (1996) studied the following neutral-neutral reaction to produce HC_5N by ab initio calculation:



They found that this reaction is exothermic without significant energy barriers. In addition, Seki et al. (1996) measured the rate coefficient of a reaction between HC_4H and CN at room temperature, and the derived value is $(4.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These results encourage the second reasoning above.

4.5. The carbon isotopic ratio in meteorites

The low value of the carbon isotopic ratio ($^{12}\text{C}/^{13}\text{C}$) obtained by HCC^{13}CN may be related to an anomaly in the carbon isotopic ratio which has been discovered in some meteorites. For example, the anomalous fraction of carbonaceous component (less than 10% of the total carbon) with an isotope ratio of 42 is known in Murchison meteorites (Swart et al. 1983). One of the reasons for this anomaly is thought to be the isotopic inhomogeneity in the proto-solar nebula. Another possibility is ^{13}C isotopic fractionation in HC_3N and possibly other carbon chain molecules in cold dark clouds before the formation of the

proto-solar nebula. A link between the carbon chain molecules and the specific fractions of carbonaceous materials in meteorites should be studied to give a more quantitative conclusion.

5. Conclusions

1. The three ^{13}C isotopomers (H^{13}CCCN , HC^{13}CCN , and HCC^{13}CN) and the normal species of HC_3N were observed in TMC-1. The spectral lines of HCC^{13}CN are significantly more intense than those of H^{13}CCCN and HC^{13}CCN , but there is no significant difference in intensities between the lines of H^{13}CCCN and HC^{13}CCN . We conclude that these differences in intensities are due to isotopic fractionation, and that this fractionation occurs in the formation processes of HC_3N , not after the HC_3N formation by the isotope exchange reaction concerning HC_3N .

2. The ratios of the abundances are 1.4 for $[\text{HCC}^{13}\text{CN}]/[\text{HC}^{13}\text{CCN}]$ and 0.95 for $[\text{H}^{13}\text{CCCN}]/[\text{HC}^{13}\text{CCN}]$. The carbon isotopic ratios, $[\text{HC}_3\text{N}]/[\text{H}^{13}\text{CCCN}]$ and $[\text{HC}_3\text{N}]/[\text{HC}^{13}\text{CCN}]$, are about 79 and 75, respectively, at the cyanopolyne peak. These isotopic ratios are close to the value in the solar neighborhood, whereas the ratio, $[\text{HC}_3\text{N}]/[\text{HCC}^{13}\text{CN}]$, is about 55. These results indicate that the ^{13}C isotope is concentrated in the CN group.

3. This fractionation is consistent with the formation processes of HC_3N by $\text{C}_2\text{H}_2^+ + \text{HCN}$, $\text{C}_2\text{H}_2 + \text{HCNH}^+$, $\text{C}_2\text{H}_2 + \text{CN}$, and/or $\text{C}_2\text{H} + \text{HNC}$ with the following two assumptions: (1) the ^{13}C isotope is concentrated in HCN , HCNH^+ , CN , and/or HNC , but not significantly in C_2H_2^+ , C_2H_2 , and/or C_2H , and (2) the CN bond in HCN , HCNH^+ , CN , and/or HNC is preserved in HC_3N . On the other hand, cyclic- C_3H_3^+ , C_3H_2^+ , and C_3H_2 cannot contribute to ^{13}C isotopic fractionation, and therefore, they cannot completely dominate for the formation of HC_3N .

4. From the limited discussion of the precursor molecules of HC_3N and isotope exchange reactions, it is probable that the CN molecule introduces the ^{13}C enriched carbon into HC_3N . Based on these results and on the reaction rate coefficients, the reaction, $\text{C}_2\text{H}_2 + \text{CN}$, is probably most important to produce HC_3N .

5. The ratio of the contributions of the two types of formation reactions which do and do not produce ^{13}C isotopic fractionation was discussed. Only when the $^{12}\text{C}/^{13}\text{C}$ ratio for HCN , HCNH^+ , CN , and/or HNC is below 43, will formation reactions which do not produce fractionation contribute more than 50%.

6. The two ^{13}C isotopomers of HC_5N ($\text{HC}^{13}\text{CCCCN}$ and $\text{HCCCC}^{13}\text{CN}$) were observed in TMC-1. A marginal difference in intensities was found.

7. The rotational excitation temperature between the NH_3 (1,1) and (2,2) levels, and the column density of NH_3 were determined to be $9.4 \pm 0.8 \text{ K}$ and $(6.5 \pm 3.0) \times 10^{14} \text{ cm}^{-2}$ (assuming the low temperature ortho/para ratio of 4), respectively, at the cyanopolyne peak.

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