The $^{12}\text{C}/^{13}\text{C}$ Ratio in Sgr B2(N): Constraints for Galactic Chemical Evolution and Isotopic Chemistry

D. T. Halfen^{1,2} , N. J. Woolf², and L. M. Ziurys^{1,2}

¹ Department of Chemistry and Biochemistry, University of Arizona, 1305 E. 4th Street, Tucson, AZ 85719, USA; halfend@email.arizona.edu

² Department of Astronomy, Arizona Radio Observatory, University of Arizona, 933 North Cherry Avenue, Tucson, AZ 85721, USA

Received 2017 April 28; revised 2017 July 18; accepted 2017 July 19; published 2017 August 22

Abstract

A study has been conducted of $^{12}\text{C}/^{13}\text{C}$ ratios in five complex molecules in the Galactic center. H_2CS , CH_3CCH , NH_2CHO , CH_2CHCN , and $\text{CH}_3\text{CH}_2\text{CN}$ and their ^{13}C -substituted species have been observed in numerous transitions at 1, 2, and 3 mm, acquired in a spectral-line survey of Sgr B2(N), conducted with the telescopes of the Arizona Radio Observatory (ARO). Between 22 and 54 individual, unblended lines for the ^{12}C species and 2–54 for ^{13}C -substituted analogs were modeled in a global radiative transfer analysis. All five molecules were found to consistently exhibit two velocity components near $V_{\text{LSR}} \sim 64$ and 73 km s^{-1} , with column densities ranging from $N_{\text{tot}} \sim 3 \times 10^{14} - 4 \times 10^{17} \text{ cm}^{-2}$ and $\sim 2 \times 10^{13} - 1 \times 10^{17} \text{ cm}^{-2}$ for the ^{12}C and ^{13}C species, respectively. Based on 14 different isotopic combinations, ratios were obtained in the range $^{12}\text{C}/^{13}\text{C} = 15 \pm 5$ to 33 ± 13 , with an average value of 24 ± 7 , based on comparison of column densities. These measurements better anchor the $^{12}\text{C}/^{13}\text{C}$ ratio at the Galactic center, and suggest a slightly revised isotope gradient of $^{12}\text{C}/^{13}\text{C} = 5.21(0.52) D_{\text{GC}} + 22.6(3.3)$. As indicated by the column densities, no preferential ^{13}C enrichment was found on the differing carbon sites of CH_3CCH , CH_2CHCN , and $\text{CH}_3\text{CH}_2\text{CN}$. Because of the elevated temperatures in Sgr B2(N), ^{13}C isotopic substitution is effectively “scrambled,” diminishing chemical fractionation effects. The resulting ratios thus reflect stellar nucleosynthesis and Galactic chemical evolution, as is likely the case for most warm clouds.

Key words: astrochemistry – Galaxy: evolution – ISM: molecules – line: identification – methods: observational – nuclear reactions, nucleosynthesis, abundances

1. Introduction

The $^{12}\text{C}/^{13}\text{C}$ isotope ratio is considered to be an important tracer of Galactic chemical evolution (GCE) because it reflects the relative degree of primary to secondary processing in stars (e.g., Chiappini & Matteucci 2001). Carbon-12 is predicted to be formed in the triple-alpha process, which fuses three He nuclei together (Timmes et al. 1995). It is thought that about 50% of ^{12}C comes from massive stars ($M > 10 M_{\odot}$) that evolve through core-collapse to become Type II supernovae (SNe II); the remaining half is from asymptotic giant branch (AGB) stars, which are intermediate mass ($1\text{--}8 M_{\odot}$) and spew out ^{12}C during the “third dredge-up.” Carbon-13, on the other hand, is a reaction intermediate in the carbon-nitrogen-oxygen (CNO) cycle, which occurs in red giants (e.g., Pagel 1997). Carbon-13 is postulated to be brought to the surface during the first and, for stars with $M > 4 M_{\odot}$, the second dredge-up, and is subsequently injected into the interstellar medium (ISM) (Herwig 2005). Because AGB stars have long evolutionary timescales relative to the age of the Galaxy, it is thought that the ^{13}C contribution to the ISM is delayed from the initial Galactic epochs. Furthermore, star formation tracks the regions of highest gas density, which occurs in the Galactic center and decreases radially. Therefore, according to GCE models, the $^{12}\text{C}/^{13}\text{C}$ ratio should increase with Galactocentric distance caused by a gradual enrichment of ^{13}C with the cycling of stellar material of all masses over the lifetime of the Galaxy (e.g., Prantzos et al. 1996).

Because of its use as a constraint of GCE, observations of the $^{12}\text{C}/^{13}\text{C}$ ratio across the Galaxy have been conducted for decades toward molecular clouds (e.g., Gardner & Whiteoak 1979; Penzias 1980; Henkel et al. 1983; Langer & Penzias 1990; Wilson & Rood 1994). The most common methods of

measuring the ratio is to compare the line intensities of rotational lines of the carbon-12 and carbon-13 isotopologues of common molecules, such as CO, H_2CO , and HCO^+ , measured by millimeter-wave astronomy. Unlike optical measurements of isotope ratios (e.g., Ritchey et al. 2011), the rotational transitions of the carbon isotopologues are well-separated in frequency. However, favorable transitions of very abundant molecules are often saturated, and therefore relative line intensities are not necessarily an accurate indicator of isotope ratios (e.g., Langer & Penzias 1990). In the past, this problem has been dealt with using molecular line modeling or double isotope ratios. More recently, CN has been used to assess this ratio because its distinct hyperfine pattern allows the opacity to be accurately evaluated (Milam et al. 2005). Possible effects of chemical fractionation may also be influencing $^{12}\text{C}/^{13}\text{C}$ ratios, arising from relative zero-point energy differences in bonds to the two isotopes.

Millimeter rotational measurements of CO, H_2CO , and CN taken over a period of several decades indicate that the $^{12}\text{C}/^{13}\text{C}$ ratio steadily increases with distance from the Galactic center (e.g., Wilson & Rood 1994; Milam et al. 2005). However, the temporal and spatial behavior of the $^{12}\text{C}/^{13}\text{C}$ ratio predicted by models adopting the standard nucleosynthesis are flatter than observations (Prantzos et al. 1996). This discrepancy has led theorists to postulate that novae (white dwarfs in binary systems) are important producers of ^{13}C , which is circulated back to the ISM on longer timescales. In addition, new carbon-13 yields for low-mass stars with cool bottom processing have been invoked (Chiappini & Matteucci 2001). However, one factor that strongly influences the proposed Galactic gradient is the ratio measured toward the Galactic center. Note that $^{12}\text{C}/^{13}\text{C}$ measurements are typically performed at $D_{\text{GC}} > 2 \text{ kpc}$, and those done near the Galactic center are subject to

self-reversal, a complex source structure, and intervening material along the line of sight (see Figure 2 of Milam et al. 2005). Therefore, the present gradient based on observations may be skewed, necessitating more accurate measurements of the $^{12}\text{C}/^{13}\text{C}$ ratio toward the Galactic center.

Not all measurements of $^{12}\text{C}/^{13}\text{C}$ ratios are suitable for Galactic gradient determinations, however. In cold, dark clouds, such as TMC-1 and L1527, carbon isotope anomalies have been observed in various long-chain molecules, e.g., HC_3N , C_4H , and C_3S (e.g., Sakai et al. 2013; Araki et al. 2016). Differing $^{12}\text{C}/^{13}\text{C}$ ratios are obtained, depending on the carbon atom. For example, in HC_3N , the $^{12}\text{C}/^{13}\text{C}$ ratio is ~ 85 – 86 if the two acetylenic carbons are considered, but the value decreases to ~ 64 for the CN moiety. These varying ratios are attributed to gas-phase chemical fractionation in formation processes, and require low temperatures near $T \sim 10$ K, as found in the starless cores in sources like TMC-1 (e.g., Araki et al. 2016). In Orion-KL, the $^{12}\text{C}/^{13}\text{C}$ ratios for HC_3N and its isotopologues vary greatly depending on the carbon atom and on the region of the cloud. These values range from 3–17 in the hot core to 27–80 in the extended ridge (Esplugues et al. 2013). In both the extended ridge and plateau, H^{13}CCCN had a $^{12}\text{C}/^{13}\text{C}$ ratio lower by about a factor of three compared to the other isotopologues. The reason for these unusual variations is unknown, although underestimation of the optical depth of the emission could be a factor.

In an effort to evaluate the abundances of organic molecules toward the Galactic center, we conducted a spectral-line survey of Sgr B2(N), using the facilities of the Arizona Radio Observatory (ARO). This source is exemplified by high densities ($>10^7 \text{ cm}^{-3}$) and temperatures (>100 K), and has at least two distinct compact cores with differing LSR velocities, one near 64 km s^{-1} (Sgr B2(N1)) and the other near 73 km s^{-1} (Sgr B2(N2); e.g., Schmiedke et al. 2016). This survey encompasses both cores, covers the majority of the 1, 2, and 3 mm atmospheric windows (160 GHz total), and was carried out at the spectral-line confusion limit. This work varies from that of Belloche et al. (2013), conducted with the IRAM 30 m, because it has 2.5 times the spectral coverage, including the 4 mm band and most of the 2 and 1 mm bands. The wide spectral coverage, although not always necessary for many projects, has enabled a large number of transitions to be measured in five lower abundance molecules, allowing an accurate evaluation of $^{12}\text{C}/^{13}\text{C}$ ratios.

The measurement of this ratio in Sgr B2(N) has been a topic of interest for years, and in particular for recent studies. For example, Müller et al. (2016) found a $^{12}\text{C}/^{13}\text{C}$ ratio of ~ 25 for both methanol and singly substituted ethanol toward Sgr B2(N2), using the Atacama Large Millimeter Array (ALMA). Also from ALMA data, Belloche et al. (2016) estimated a ratio of ~ 21 from CH_3CN , based on both carbon atoms, and the value of ~ 32 from ethyl cyanide considering all three carbon-substitutions, for Sgr B2(N2). From IRAM data, Belloche et al. found $^{12}\text{C}/^{13}\text{C} \sim 30$ from $\text{C}_2\text{H}_5\text{CN}$, based on all three ^{13}C -substitutions, considering both hot cores. An intensive ALMA study of ethyl cyanide, including both singly substituted and doubly substituted ^{13}C isotopologues, by Margulès et al. (2016), suggested a $^{12}\text{C}/^{13}\text{C}$ ratio near ~ 25 for Sgr B2(N2).

In this paper, we present our $^{12}\text{C}/^{13}\text{C}$ ratio measurements toward Sgr B2(N) from our single-dish survey. We discuss

their implications for GCE, as well as possible consequences for isotopologue chemistry in hot cores of molecular clouds.

2. Observations

The data were obtained as part of a spectral-line survey of the 1, 2, and 3 mm windows toward Sgr B2(N). These spectra were recorded during the period 2002 September to 2013 April using the Arizona Radio Observatory (ARO) 12 m telescope on Kitt Peak and the Submillimeter Telescope (SMT) on Mt. Graham. At the 12 m, the detectors were millimeter-wave receivers using dual-polarization, SIS mixers, which cover the 3 and 2 mm bands (68–116 and 130–172 GHz). These mixers were operated in single-sideband (SSB) mode with typical image sideband rejection of ≥ 18 dB. The temperature scale was established using the chopper wheel method, corrected for forward spillover losses, and is given as T_R^* . The radiation temperature T_R , assuming the source fills only the main beam, is $T_R = T_R^*/\eta_c$, where η_c is the main-beam efficiency corrected for forward spillover losses. A millimeter-wave autocorrelator (MAC) backend was employed for these measurements with either 390 kHz or 781 kHz resolution and 600 MHz bandwidth per polarization. The spectra were smoothed using a cubic spline routine to a 1 MHz resolution.

At the SMT, data were obtained in the 210–280 GHz (1 mm) range with a dual-polarization receiver that employs ALMA Band 6 sideband-separating (SBS) mixers, typically with image rejection ≥ 16 dB. The temperature scale is given as T_A^* , and the radiation temperature T_R is $T_R = T_A^*/\eta_b$, where η_b is the main-beam efficiency. A 1 MHz resolution filter bank with 2048 channels was the spectrometer backend, configured in parallel mode (2×1024).

The beam size ranged from $92''$ to $37''$ at the 12 m and $32''$ to $27''$ at the SMT; see Table 1. All observations were conducted toward Sgr B2(N) ($\alpha = 17^{\text{h}}44^{\text{m}}09^{\text{s}}.5$; $\delta = -28^\circ21'20''$; B1950.0, or $\alpha = 17^{\text{h}}47^{\text{m}}19^{\text{s}}.2$; $\delta = -28^\circ22'22''$; J2000.0: NED <http://ned.ipac.caltech.edu/forms/calculator.html>) in position-switching mode with a $+30'$ OFF position in azimuth. Any image contamination was identified using a 10–20 MHz local oscillator shift and direct observation of the image sideband. The pointing accuracy was $\pm 5''$ – $10''$ at the 12 m and $\pm 1''$ – $2''$ at the SMT. The telescope pointing was determined by observations of planets.

3. Results and Analysis

3.1. Overview of Molecules Studied

The five molecules chosen for this investigation, H_2CS , CH_3CCH , NH_2CHO , CH_2CHCN , and $\text{CH}_3\text{CH}_2\text{CN}$, contain carbon in differing functional groups. Table 1 summarizes the carbon isotopologues studied, the number of transitions detected (22–54 lines for the ^{12}C species and 2–54 for ^{13}C -substituted), the energy range of the lower state levels, typical line widths and LSR velocities, and the average rotational temperature and column density. As the table shows, each molecule exhibits two distinct velocity components near 62–64 (hot core Sgr B2(N1)) and 73 km s^{-1} (hot core Sgr B2(N2)) with typical line widths of 9–14 km s^{-1} . Additional details will be given in a later paper on the entire survey.

A representative sample of the observational data is given in Table 2, which lists the complete data set for H_2CS and H_2^{13}CS . For H_2CS , 33 lines were observed that were uncontaminated; these transitions are shown in the table. The rest frequency, the

Table 1
Modeling Results for Observed Molecules

Species	Transitions Detected	E_l Range (cm ⁻¹)	$\Delta V_{1/2}$ (km s ⁻¹)	V_{LSR} (km s ⁻¹)	θ_s^a (arcsec)	T_{rot} (K)	N_{tot} (cm ⁻²)
H ₂ CS	54	1–252	14.0 ^a	63.4	^b	71 ± 19	6.9 ± 1.8 × 10 ¹⁴
	54	1–252	14.0 ^a	73.0 ^a	^b	75 ^b	2.8 ± 0.8 × 10 ¹⁴
H ₂ ¹³ CS	2	12–20	14.0 ^a	64.0 ^a	^b	88 ± 19	3.7 ± 0.8 × 10 ¹³
	2	12–20	14.0 ^a	73.0 ^a	^b	86 ± 18	1.9 ± 0.4 × 10 ¹³
CH ₃ CCH	28	3–113	10.0 ^a	63.0	^b	59 ± 13	2.2 ± 0.5 × 10 ¹⁵
	28	3–113	10.0 ^a	73.0 ^a	^b	68 ± 14	1.5 ± 0.3 × 10 ¹⁵
¹³ CH ₃ CCH	3	5–26	10.0 ^a	64.0 ^a	^b	72 ± 12	9.1 ± 1.5 × 10 ¹³
	3	5–26	10.0 ^a	73.0 ^a	^b	72 ± 12	8.3 ± 1.4 × 10 ¹³
CH ₃ C ¹³ CH	4	8–53	10.0 ^a	64.0 ^a	^b	74 ± 13	1.1 ± 0.2 × 10 ¹⁴
	4	8–53	10.0 ^a	73.0 ^a	^b	74 ± 13	6.8 ± 1.2 × 10 ¹³
NH ₂ CHO	22	0–83	10.0 ^a	63.0	45.0	150 ± 26	3.1 ± 0.5 × 10 ¹⁵
	22	0–83	10.0 ^a	73.0 ^a	45.0	148 ± 26	1.6 × 10 ^{15a}
NH ₂ ¹³ CHO	16	4–57	10.0 ^a	64.0 ^a	45.0	150 ± 41	1.2 ± 0.3 × 10 ¹⁴
	16	4–57	10.0 ^a	73.0 ^a	45.0	150 ± 41	5.2 ± 1.4 × 10 ¹³
¹³ CH ₂ CHCN	42	13–296	10.4	63.1	1.0	80 ± 29	6.9 ± 2.5 × 10 ¹⁶
	42	13–296	10.0 ^a	73.0 ^a	1.0	80 ± 29	1.2 ± 0.4 × 10 ¹⁶
CH ₂ ¹³ CHCN	21	10–312	9.3	62.4	1.0	80 ± 17	8.6 ± 1.9 × 10 ¹⁶
	21	10–312	10.0 ^a	73.0 ^a	1.0	80 ± 17	3.3 ± 0.7 × 10 ¹⁶
CH ₂ CH ¹³ CN	30	13–198	9.5	64.0	1.0	80 ± 27	1.3 ± 0.4 × 10 ¹⁷
	30	13–198	10.0 ^a	73.0 ^a	1.0	80 ± 27	2.2 ± 0.8 × 10 ¹⁶
CH ₃ CH ₂ CN	53	9–303	12.0 ^a	64.0 ^a	3.0	86 ± 28	4.1 ± 1.3 × 10 ¹⁷
	53	9–303	12.0 ^a	73.0 ^a	3.0	86 ± 27	2.5 × 10 ^{17a}
¹³ CH ₃ CH ₂ CN	54	9–141	12.0 ^a	60.1	3.0	90 ± 24	1.9 ± 0.5 × 10 ¹⁶
	54	9–141	12.0 ^a	73.0 ^a	3.0	91 ± 24	1.2 ± 0.3 × 10 ¹⁶
CH ₃ ¹³ CH ₂ CN	47	11–139	12.0 ^a	61.9	3.0	85 ± 20	1.2 ± 0.3 × 10 ¹⁶
	47	11–139	12.0 ^a	73.0 ^a	3.0	86 ± 20	1.0 ± 0.2 × 10 ¹⁶
CH ₃ CH ₂ ¹³ CN	52	9–183	12.8	61.3	3.0	87 ± 24	1.4 ± 0.4 × 10 ¹⁶
	52	9–183	12.0 ^a	73.0 ^a	3.0	85 ± 23	8.8 ± 2.4 × 10 ¹⁵

Notes.

^a Held fixed in fit.

^b Source fills telescope beam.

upper state energy (E_u), and the product of the square of the dipole moment μ with the line strength ($\mu^2 S$) of the transition are also given, along with the beam efficiency (η_c at 2 and 3 mm and η_b at 1 mm) and telescope beam size. The line temperature (T_R^* at 2 and 3 mm and T_A^* at 1 mm), line width $\Delta V_{1/2}$, and source velocity V_{LSR} are also given for each velocity component. At 3 mm in wavelength, these components are usually blended, producing a line with a width of ~ 20 km s⁻¹. At 2 and 1 mm, the two components usually generate a distinct profile with a prominent feature at 64 km s⁻¹ and a weaker “shoulder” near 73 km s⁻¹.

Representative spectra from Sgr B2(N) for each isotopologue of the five respective molecules, both the ¹²C and ¹³C species, are shown in Figures 1(a) and (b). Here the black trace is the observed data, while the red line is the current model fit (see below). The features of interest are indicated with arrows. The top three panels in Figure 1(a) show one line of H₂CS and two for H₂¹³CS near 104.6, 97.6, and 162.7 GHz, respectively, while the next two graphs present data for NH₂CHO and NH₂¹³CHO near 140.6 and 169.0 GHz. The lower three panels in Figure 1(a) show various K components ($K = 0$ –3 or 4) of transitions of CH₃CCH (102.5 GHz), ¹³CH₃CCH (83.1 GHz), and CH₃C¹³CH (99.4 GHz). The $K = 0$, 1, and 2 components are typically blended together into a single asymmetric feature for these species. Unfortunately, all lines for CH₃¹³CCH were contaminated either by those of the main isotopologue or by other molecules; accurate spectral parameters could not be determined for this species.

The H₂¹³CS and NH₂¹³CHO spectra (second and fifth panels, Figure 1(a)) illustrate the evolution of the line shape as a function of frequency. The two velocity components are collapsed into one single feature in the 97.6 GHz line. For the formamide-¹³C transition at 169.0 GHz, a shoulder at higher velocity (~ 73 km s⁻¹) can be seen on the “main” (64 km s⁻¹) line.

In Figure 1(b), the top four panels show representative spectra for the ¹²C and singly substituted ¹³C isotopologues of vinyl cyanide (CH₂CHCN: 94.9 GHz; ¹³CH₂CHCN: 110.9 GHz; CH₂¹³CHCN: 103.8 GHz; and CH₂CH¹³CN: 94.5 GHz). In the lower four panels, the ¹²C and singly substituted ¹³C species of ethyl cyanide (CH₃CH₂CN: 93.8 GHz; ¹³CH₃CH₂CN: 96.1 GHz; CH₃¹³CH₂CN: 98.1 GHz; and CH₃CH₂¹³CN: 112.1 GHz) are displayed. In each spectrum, typical multiple (a -type) transitions of the respective isotopologue are visible, as indicated again by arrows. Some transitions $J + 1, K_a \rightarrow J, K_a$ lie at the same frequency, differentiated only by changes in the K_c quantum number. In these cases, K_c is substituted by an asterisk in the figure.

3.2. Analysis Method

The data sets for the five molecules across the 1, 2, and 3 mm bands were analyzed in a global fit using a radiative code. In this algorithm, observed spectra are simulated by varying the values of the line width and LSR velocity, as well as the rotational temperature, total column density, and source size. The “best fit” is established by a nonlinear least-squares

Table 2
Representative Data: Observations of H₂CS and H₂¹³CS in Sgr B2(N)

Species	Transition $J'_{K_a, K_c} \rightarrow J''_{K_a, K_c}$	Frequency (MHz)	E_u (K)	$\mu^2 S(D^2)$	η_c/η_b	$\theta_b(^{\circ})$	V_{LSR} (km s ⁻¹)	T_R^*/T_A^* (K)	$\Delta V_{1/2}$ (km s ⁻¹)
H ₂ CS	2 _{0,2} → 1 _{0,1}	68699.38	4.95	5.43	0.94	92	63.7	0.375	14.0
							72.4	0.357	14.0
	2 _{1,1} → 1 _{1,0}	69746.75	18.20	12.21	0.94	90	65.2	0.555	14.0
							73.8	0.523	14.0
	3 _{1,3} → 2 _{1,2}	101477.81	22.92	21.70	0.88	62	64.4	1.030	14.0
							73.3	0.880	14.0
	3 _{2,2} → 2 _{2,1}	103039.91 ^a	62.59	4.52	0.87	61	62.5	0.691	14.0
	3 _{0,3} → 2 _{0,2}	103040.45 ^a	9.90	8.14	0.87	61	74.2	0.480	14.0
	3 _{2,1} → 2 _{2,0}	103051.85	62.60	4.52	0.87	61	64.5	0.210	14.0
							73.2	0.145	14.0
	3 _{1,2} → 2 _{1,1}	104617.04	23.23	21.70	0.87	60	62.1	0.962	14.0
							73.6	0.714	14.0
	4 _{1,4} → 3 _{1,3}	135298.26	29.42	30.52	0.79	46	62.6	1.306	14.0
							73.7	0.760	14.0
	4 _{3,2} → 3 _{3,1}	137369.49 ^a	135.01	14.24	0.79	46	62.1	1.108	14.0
	4 _{3,1} → 3 _{3,0}	137369.49 ^a	135.01	14.24	0.79	46	73.0	0.647	14.0
	4 _{0,4} → 3 _{0,3}	137371.21 ^a	16.49	10.85	0.79	46			
	4 _{2,3} → 3 _{2,2}	137382.12	69.19	8.14	0.79	46	64.4	0.403	14.0
							73.2	0.346	14.0
	4 _{2,2} → 3 _{2,1}	137412.01	69.19	8.14	0.79	46	64.2	0.310	14.0
							72.9	0.235	14.0
	4 _{1,3} → 3 _{1,2}	139483.68	29.92	30.52	0.78	45	63.5	1.433	14.0
							72.1	0.979	14.0
	5 _{1,4} → 4 _{1,4}	169114.08	37.54	39.06	0.70	37	63.9	1.712	14.0
							72.8	0.981	14.0
	5 _{4,2} → 4 _{4,1}	171670.98 ^a	235.31	4.88	0.69	37	62.0	0.141	14.0
	5 _{4,1} → 4 _{4,0}	171670.98 ^a	235.31	4.88	0.69	37	72.4	0.050	14.0
	5 _{0,5} → 4 _{0,4}	171688.12	24.74	13.56	0.69	37	64.0	0.927	14.0
							72.7	0.569	14.0
	5 _{2,3} → 4 _{2,2}	171780.17	77.44	11.39	0.69	37	64.0	0.483	14.0
							72.8	0.263	14.0
	7 _{1,7} → 6 _{1,6}	236727.02	58.66	55.81	0.75	32	64.6	1.909	14.0
							73.4	1.106	14.0
	7 _{5,3} → 6 _{5,2}	240261.99 ^a	374.93	27.92	0.75	31	61.5	1.220	14.0
	7 _{5,2} → 6 _{5,1}	240261.99 ^a	374.93	27.92	0.75	31	72.8	0.420	14.0
	7 _{0,7} → 6 _{0,6}	240266.87 ^a	46.17	18.99	0.75	31			
	7 _{2,6} → 6 _{2,5}	240382.05 ^a	98.88	17.44	0.75	31	64.5	1.355	14.0
	7 _{3,5} → 6 _{3,4}	240393.04 ^a	164.70	46.51	0.75	31	73.3	1.024	14.0
	7 _{3,4} → 6 _{3,3}	240393.76 ^a	164.70	46.51	0.75	31			
	7 _{2,5} → 6 _{2,4}	240549.07	98.90	17.44	0.75	31	65.8	0.644	14.0
							73.3	0.456	14.0
	7 _{1,6} → 6 _{1,5}	244048.50	60.06	55.80	0.75	31	63.8	2.013	14.0
							73.7	0.925	14.0
	8 _{1,8} → 7 _{1,7}	270521.93	71.65	64.09	0.75	28	64.1	1.904	14.0
							73.0	0.986	14.0
	8 _{2,7} → 7 _{2,6}	274703.35	112.07	20.35	0.75	27	64.6	0.481	14.0
							73.3	0.290	14.0
	8 _{3,6} → 7 _{3,5}	274732.98 ^a	177.89	55.96	0.75	27	63.8	1.080	14.0
	8 _{3,5} → 7 _{3,4}	274734.40 ^a	177.89	55.96	0.75	27	73.7	0.459	14.0
	8 _{2,6} → 7 _{2,5}	274953.74	112.10	20.35	0.75	27	63.9	0.769	14.0
							72.6	0.558	14.0
H ₂ ¹³ CS	3 _{1,3} → 2 _{1,2}	97632.20	22.55	21.72	0.89	64	62.6	0.055	14.0
							71.8	0.033	14.0
	5 _{1,5} → 4 _{1,4}	162706.57	36.62	39.10	0.71	39	63.1	0.061	14.0
							72.3	0.028	14.0

Notes. Source coordinates (B1950): $\alpha = 17^{\text{h}}44^{\text{m}}09^{\text{s}}.5$, $\delta = -28^{\circ}21'20''$. Spectra were observed with the Millimeter Auto Correlator (MAC) and resampled at 1 MHz resolution using a standard cubic spline algorithm. Line parameters were derived from a least-squares fit of a Gaussian profile to the spectrum.

^a Lines compose one feature with given values of V_{LSR} .

Figure 1. Representative spectra of ^{12}C and ^{13}C species measured toward Sgr B2(N) with the ARO 12 m telescope at 3 and/or 2 mm. Individual lines of the carbon isotopologues of (a) H_2CS , CH_3CCH , and NH_2CHO , (b) CH_2CHCN and $\text{CH}_3\text{CH}_2\text{CN}$ are shown, indicated by arrows underneath the data. The spectral resolution is 1 MHz. The central frequency of each spectrum and quantum numbers of transitions are indicated for each panel, assuming an LSR velocity of 64 km s^{-1} . Multiple K_c quantum numbers for series of asymmetry components for CH_2CHCN and $\text{CH}_3\text{CH}_2\text{CN}$ are indicated by asterisks (e.g., $J_{K_a K_c} = 10_{7,3} \rightarrow 9_{7,2}$ and $10_{7,4} \rightarrow 9_{7,3}$ is shown as $10_{7,*} \rightarrow 9_{7,*}$). The modeled spectrum overlays the data in red, assuming two velocity components near 64 and 73 km s^{-1} . The approximate integration time per spectrum is 4–16 hr.

evaluation. For some of the weaker isotopologues, certain free parameters had to be fixed to a given value, as described in the next section. The line shapes were assumed to be Gaussian. Rest frequencies, level energies, line strengths ($\mu^2 S$),

and partition functions were obtained from spectral-line databases.

In the analysis, a global fit was first carried out of the entire Sgr B2(N) data set, assuming the source fills the telescope

Figure 2. Plot of the $^{12}\text{C}/^{13}\text{C}$ isotope ratio as a function of distance to the Galactic center, D_{GC} (kpc), using the data of Table 2 of Milam et al. (2005) and the new values from this work. The solar distance to the Galactic center is assumed to be 7.9 kpc. The revised gradient is $^{12}\text{C}/^{13}\text{C} = 5.21(0.52) D_{\text{GC}} + 22.6(3.3)$.

beam. This fitting enabled the identification of obvious blended lines for a given species, which were then removed from the analysis. All uncontaminated transitions for a given molecule and its ^{13}C isotopologues were then analyzed separately. For two species, H_2CS and CH_3CCH , the assumptions of low opacity and extended emission were excellent approximations, and the observed lines were well modeled. The extended emission of these two molecules is apparent in the $5' \times 5'$ maps, centered on Sgr B2(N), made by the Mopra telescope (Jones et al. 2008). For the other three molecules (NH_2CHO , CH_2CHCN , and $\text{CH}_3\text{CH}_2\text{CN}$), many transitions in the main isotopologue were optically thick, and the emission appeared more confined with respect to the telescope beam. Because the source size and line opacities are very highly correlated, it was difficult to fit the optically thick transitions with sufficient confidence to determine accurate $^{12}\text{C}/^{13}\text{C}$ ratios.

For NH_2CHO and $\text{CH}_3\text{CH}_2\text{CN}$, this situation was remedied by fitting the numerous optically thin b -type lines of the main isotopic species, and adjusting the source size. Unfortunately, CH_2CHCN exhibits a small number of such transitions, which also have weak intensities. Consequently, only the ^{13}C species were confidently modeled. Note that the line profiles of all five species were successfully fit with line widths between 9 and 14 km s^{-1} and two LSR components near 64 and 73 km s^{-1} . To arrive at an estimate of the source sizes for NH_2CHO , $\text{CH}_3\text{CH}_2\text{CN}$, and CH_2CHCN , the line intensities were first compared to lines measured with the IRAM 30 m telescope. This value was used as an initial guess and then varied systematically until the best size was established by the least-squares analysis. Once determined, the source size was held fixed in the final fit, which established the rotational temperature and column density. This approach was necessary because the source size, rotational temperature, and column density are highly correlated (96%–99%) in the analysis. One parameter had to be held constant in order for the others to have significant values.

The results of this analysis are given in Table 1 and the simulated spectra for Sgr B2(N) are shown in red in Figure 1, as mentioned. Details for each molecule are outlined in the next section.

3.3. Results for Individual Molecules

3.3.1. Thioformaldehyde (H_2CS and H_2^{13}CS)

The CDMS entries (046509 ver. 2 and 047505 ver. 1) were used to evaluate both the H_2CS and H_2^{13}CS spectra (Endres et al. 2016). The database entries are based on the spectroscopy work of Maeda et al. (2008). Thirty-three lines of H_2CS were modeled, assuming the source fills the main beam and fixing line widths to $\Delta V_{1/2} = 14.0 \text{ km s}^{-1}$. The velocity of one component was varied, yielding $V_{\text{LSR}} = 63.4 \text{ km s}^{-1}$, while the other was fixed to $V_{\text{LSR}} = 73.0 \text{ km s}^{-1}$. The rotational temperature of the 63.4 km s^{-1} component was successfully modeled with $T_{\text{rot}} = 71 \text{ K}$, while the other was fixed to $T_{\text{rot}} = 75 \text{ K}$. The corresponding total column densities of the two velocity components were determined to be $N_{\text{tot}} \sim 6.9 \times 10^{14}$ and $2.8 \times 10^{14} \text{ cm}^{-2}$ (see Table 1).

Two distinct lines of H_2^{13}CS were detected near 97.6 and 162.7 GHz. Consequently, the spectra were modeled with the line parameters fixed to those found for the ^{12}C isotopologue ($\Delta V_{1/2} = 14.0 \text{ km s}^{-1}$ and $V_{\text{LSR}} = 64.0$ and 73.0 km s^{-1}). The 64 km s^{-1} component was found to have $T_{\text{rot}} = 88 \text{ K}$ and $N_{\text{tot}} \sim 3.7 \times 10^{13} \text{ cm}^{-2}$, while the 73.0 km s^{-1} feature exhibited $T_{\text{rot}} = 86 \text{ K}$ and $N_{\text{tot}} \sim 1.9 \times 10^{13} \text{ cm}^{-2}$. The rotational temperatures are in reasonable agreement with those of the ^{12}C species. Comparing column densities, $^{12}\text{C}/^{13}\text{C} \sim 19 \pm 6$ and 15 ± 5 for the 64.0 and 73.0 km s^{-1} components, respectively (see Table 3).

In their survey of Sgr B2, Belloche et al. (2013) observed lines of H_2CS , but did not have a definitive detection of H_2^{13}CS . They modeled their main isotope data at 3 mm with two very similar velocity components with 8 km s^{-1} line widths, and a third, less certain feature near 54 km s^{-1} . We do not see this lower velocity gas in our data. These authors fit

Table 3
Summary of Derived $^{12}\text{C}/^{13}\text{C}$ Ratios

^{12}C Species	^{13}C Species	V_{LSR} (km s $^{-1}$)	$^{12}\text{C}/^{13}\text{C}$
H_2CS	H_2^{13}CS	64.0	19 ± 6
		73.0	15 ± 5
CH_3CCH	$^{13}\text{CH}_3\text{CCH}$	64.0	24 ± 7
		73.0	18 ± 5
CH_3CCH	$\text{CH}_3\text{C}^{13}\text{CH}$	64.0	19 ± 5
		73.0	22 ± 6
NH_2CHO	$\text{NH}_2^{13}\text{CHO}$	64.0	25 ± 8
		73.0	31 ± 8
$\text{CH}_3\text{CH}_2\text{CN}$	$^{13}\text{CH}_3\text{CH}_2\text{CN}$	62.1	21 ± 9
		73.0	20 ± 5
$\text{CH}_3\text{CH}_2\text{CN}$	$\text{CH}_3^{13}\text{CH}_2\text{CN}$	62.7	33 ± 13
		73.0	24 ± 6
$\text{CH}_3\text{CH}_2\text{CN}$	$\text{CH}_3\text{CH}_2^{13}\text{CN}$	62.1	29 ± 12
		73.0	28 ± 8
Average		64.0	24 ± 9
		73.0	23 ± 6

their spectra with both hot and cold components and with a source size of a few arcseconds, but commented that their resulting line parameters were not well constrained. Our data were well modeled with an extended source and a single temperature component, which may simply reflect our larger beam size.

3.3.2. Methylacetylene (CH_3CCH , $^{13}\text{CH}_3\text{CCH}$, and $\text{CH}_3\text{C}^{13}\text{CH}$)

The JPL database entries were used in the analysis of the three observed isotopologues of methylacetylene CH_3CCH (or propyne: 040001, 041004, and 41002, all ver. 1; Pickett et al. 1998), all based on the experiment work of Dubrulle et al. (1978). Because of two velocity components and a ~ 10 km s $^{-1}$ line width, lower value K components were typically blended to create a single asymmetric feature for all three species, see Figure 1(a). However, the line shapes could be well reproduced for all isotopologues by fixing the line widths to the 10 km s $^{-1}$ value and the V_{LSR} velocity of one of the two components to 73.0 km s $^{-1}$. The other velocity was varied to obtain the best fit, yielding values of 63–64 km s $^{-1}$.

In the analysis of the main isotopologue CH_3CCH , 28 transitions were fit across the 3, 2, and 1 mm regions up to $K = 5$. The analysis yielded rotational temperatures of 59 and 68 K for the $V_{\text{LSR}} = 64.0$ and 73.0 km s $^{-1}$ components, respectively, with column densities of $N_{\text{tot}} = 2.2 \times 10^{15}$ and 1.5×10^{15} cm $^{-2}$, assuming the source filled the beam. This assumption is supported by Jones et al. (2008), who mapped this species across Sgr B2, which showed extended emission of this molecule. As mentioned, only two of the three possible ^{13}C isotopologues were clearly detected, $^{13}\text{CH}_3\text{CCH}$ and $\text{CH}_3\text{C}^{13}\text{CH}$, with one rotational transition $J + 1 \rightarrow J$ per species near 83.1 and 99.5 GHz, respectively, each consisting of 3–4 K components (see Figure 1(a)). The third isotopologue $\text{CH}_3^{13}\text{CCH}$, was not analyzed because of line contamination, as mentioned. The rotational temperatures for $^{13}\text{CH}_3\text{CCH}$ and $\text{CH}_3\text{C}^{13}\text{CH}$ were determined to be 72 and 74 K, applicable to both velocity components. The column densities for the 64.0 and 73.0 km s $^{-1}$ features were established to be $N_{\text{tot}} = 9.1 \times 10^{13}$ and 8.3×10^{13} cm $^{-2}$ for $^{13}\text{CH}_3\text{CCH}$, and 1.1×10^{14} and 6.8×10^{13} cm $^{-2}$ for $\text{CH}_3\text{C}^{13}\text{CH}$, respectively.

These values yield $^{12}\text{C}/^{13}\text{C}$ ratios for the 64.0 and 73.0 km s $^{-1}$ components of 24 ± 7 and 18 ± 5 from $^{13}\text{CH}_3\text{CCH}$, and, using $\text{CH}_3\text{C}^{13}\text{CH}$, 19 ± 5 and 22 ± 6 , as displayed in Table 3.

Belloche et al. (2013) only measured a single line for each of the ^{13}C isotopologues. They did not calculate a $^{12}\text{C}/^{13}\text{C}$ ratio, but assumed a value of 20 to estimate abundances of the ^{13}C species. These authors chose an arbitrary source size of $10''$ for CH_3CCH , and fit their 3 mm data with two velocity components that are almost identical to those used here. They noted that their chosen source size was not compatible with Mopra data, which for CH_3CCH showed extended emission across several arcminutes (Jones et al. 2008).

3.3.3. Formamide (NH_2CHO and $\text{NH}_2^{13}\text{CHO}$)

In the analysis of NH_2CHO and $\text{NH}_2^{13}\text{CHO}$, the CDMS entries (045512 and 046512, both ver. 2) were employed, based on the work of Motiyenko et al. (2012). Twenty-two fully resolved b -type transitions of NH_2CHO and 16 a -type lines of $\text{NH}_2^{13}\text{CHO}$ were modeled. A large number of the a -type lines were identified for the main isotopic species but were not used in the analysis, as mentioned. The data for both species were fit with the usual two velocity components and a fixed line width of 10 km s $^{-1}$. For NH_2CHO , the LSR velocity of one component was fixed to 73.0 km s $^{-1}$, while the other velocity was determined to be 63.4 km s $^{-1}$ from the fit; both LSR velocities were fixed for the ^{13}C species to 64.0 and 73.0 km s $^{-1}$. A source size of $45''$ was estimated by comparison of the relative intensities of the lines from the 12 m and IRAM 30 m. This source size is consistent with the Mopra maps of the Sgr B2(N) region from Jones et al. (2008), although their image is contaminated by H_2COH^+ . The rotational temperature of NH_2CHO was determined to be 150 and 148 K for the 64 and 73 km s $^{-1}$ features, respectively, with column densities of 3.1×10^{15} and 1.6×10^{15} cm $^{-2}$. For $\text{NH}_2^{13}\text{CHO}$, the rotational temperature was estimated to be $T_{\text{rot}} \sim 150$ K for both components; column densities slightly varied with $N_{\text{tot}} \sim 1.2 \times 10^{14}$ for the 63 km s $^{-1}$ feature and 5.2×10^{13} cm $^{-2}$ for that at 73 km s $^{-1}$. The subsequent $^{12}\text{C}/^{13}\text{C}$ ratios are then 25 ± 8 and 31 ± 8 for the two velocity components, see Table 3.

Both ^{12}C and ^{13}C species were observed by Belloche et al. (2013), but no ratio was calculated. They analyzed their formamide data at 3 mm with three velocity components, two that are identical to ours, and a weaker third feature near 80 km s $^{-1}$. The optically thick main isotopic lines were included in their modeling, which used a source size of a few arcseconds. This source size is not consistent with the Mopra map of this molecule (Jones et al. 2008), suggesting the observations of Belloche et al. are less sensitive to extended formamide emission and more to emission associated with the two hot cores as compared to our observations, which can be explained naturally by the different beam sizes.

3.3.4. Vinyl Cyanide (CH_2CHCN , $^{13}\text{CH}_2\text{CHCN}$, $\text{CH}_2^{13}\text{CHCN}$, and $\text{CH}_2\text{C}^{13}\text{CHCN}$)

For the analysis of the isotopologues of vinyl cyanide, the CDMS data (053515, 054506, 054507, and 054508, all ver. 1) were used. These entries are based on laboratory work by Gerry & Winnewisser (1973), Baskakov et al. (1996), and Cazzoli & Kisiel (1988) for the main isotopic species and Colmont et al. (1997) for the ^{13}C isotopologues. For CH_2CHCN , most lines

were optically thick and were not modeled, as previously discussed.

For $^{13}\text{CH}_2\text{CHCN}$, $\text{CH}_2^{13}\text{CHCN}$, and $\text{CH}_2\text{CH}^{13}\text{CN}$, 42, 21, and 30 uncontaminated lines were analyzed, all containing the two velocity components. Comparing the line intensities of these species with those of the IRAM 30 m suggested a $\sim 1''$ source size, which was then assumed in the analysis. For all three ^{13}C species, the higher velocity component V_{LSR} was fixed to 73.0 km s^{-1} in the modeling, while the LSR velocity of the other feature was varied, the best fit resulting in values of $V_{\text{LSR}} = 63.1, 62.4, \text{ and } 64.0 \text{ km s}^{-1}$ for $^{13}\text{CH}_2\text{CHCN}$, $\text{CH}_2^{13}\text{CHCN}$, and $\text{CH}_2\text{CH}^{13}\text{CN}$, respectively. For the 73 km s^{-1} component, line widths were fixed to $\Delta V_{1/2} = 10 \text{ km s}^{-1}$, while optimizing the fit produced values of 10.4, 9.3, and 9.5 km s^{-1} for the 64 km s^{-1} feature. The rotational temperatures were determined in the analysis to be $\sim 80 \text{ K}$ for all three species. The column densities of the 64 km s^{-1} component were in the range $N_{\text{tot}} \sim 0.7\text{--}1.3 \times 10^{17} \text{ cm}^{-2}$, while at 73.0 km s^{-1} , these values were lower with $N_{\text{tot}} \sim 1.2\text{--}3.3 \times 10^{16} \text{ cm}^{-2}$ (see Table 1).

In their analysis of vinyl cyanide, Belloche et al. (2013) used a fit with three velocity components—two identical to those found here. The third is the lower velocity feature with $V_{\text{LSR}} \sim 54\text{--}55 \text{ km s}^{-1}$, which they also observed in H_2CS . These authors modeled their data with a source size of $1''\text{--}3''$ and included optically thick transitions for the main isotopologue. Their derived column densities for the ^{13}C species are very similar to those determined here. Overall, the agreement between the two analyses is good, considering the uncertainties. Previously, Müller et al. (2008) had detected all three ^{13}C species of vinyl cyanide with ALMA, as mentioned, and estimated $^{12}\text{C}/^{13}\text{C} \sim 21$ for Sgr B2(N2), while Belloche et al. (2016) found a ratio of 20 for the same core, using ALMA observations of this species. These ratios are consistent with our values from other molecules.

3.3.5. Ethyl Cyanide ($\text{CH}_3\text{CH}_2\text{CN}$, $^{13}\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3^{13}\text{CH}_2\text{CN}$, and $\text{CH}_3\text{CH}_2^{13}\text{CN}$)

The CDMS entries (055502, 056506, 056505, and 056504, all ver. 2) were employed to analyze the ^{12}C and ^{13}C species of ethyl cyanide in Sgr B2(N). The data for $\text{CH}_3\text{CH}_2\text{CN}$ are from Brauer et al. (2009) and Fukuyama et al. (1996), while Richard et al. (2013) measured the spectrum of the ^{13}C isotopologues. A source size of $3''$ was assumed, determined by comparison of intensities with the IRAM 30 m data. For the ^{12}C isotopologue, 53 b -type transitions were analyzed in Sgr B2(N) to establish the abundance. A two-component model was used, as per the other molecules studies here, and both the LSR velocities and line widths were fixed to $V_{\text{LSR}} = 64.0 \text{ and } 73.0 \text{ km s}^{-1}$, with $\Delta V_{1/2} = 12.0 \text{ km s}^{-1}$. The subsequent fit resulted in $T_{\text{rot}} \sim 86 \text{ K}$, with $N_{\text{tot}}(64 \text{ km s}^{-1}) \sim 4.1 \times 10^{17} \text{ cm}^{-2}$, while $N_{\text{tot}}(73 \text{ km s}^{-1})$ was fixed to $2.5 \times 10^{17} \text{ cm}^{-2}$.

For the ^{13}C isotopologues, 54, 47, and 52 uncontaminated lines from a -type transitions were analyzed with the two velocity components. The line widths were held fixed to $\Delta V_{1/2} = 12.0 \text{ km s}^{-1}$ for both velocity features in all three species, except for the 64 km s^{-1} component in $\text{CH}_3\text{CH}_2^{13}\text{CN}$. In this case, it was varied, yielding a best fit of 12.8 km s^{-1} . One LSR velocity was fixed to 73.0 km s^{-1} , and the other was a free parameter, resulting in fitted values of $V_{\text{LSR}} \sim 60.1\text{--}61.9 \text{ km s}^{-1}$. The quality of the fit was quite good for these species, as shown in Figure 1(b). The resulting rotational

temperatures were in the range of $T_{\text{rot}} \sim 85\text{--}91 \text{ K}$ for the ^{13}C isotopologues, with $N_{\text{tot}} \sim 1.2\text{--}1.9 \times 10^{16} \text{ cm}^{-2}$ for the lower velocity gas and $N_{\text{tot}} \sim 0.88\text{--}1.2 \times 10^{16} \text{ cm}^{-2}$ for the higher velocity material: see Table 1. The $^{12}\text{C}/^{13}\text{C}$ ratio was found to be in the range 20 ± 5 to 33 ± 13 for the isotopic combinations for both velocity components (see Table 3).

In their survey, Belloche et al. (2013) observed all three ^{13}C species for ethyl cyanide, as well as the main isotopologue. They fit both optically thin and thick transitions at 3 mm, assuming a source size of $2''\text{--}3''$ with 55, 63, and 73 km s^{-1} velocity components. Their resulting column densities agree well with those determined here. In this case, they estimated $^{12}\text{C}/^{13}\text{C} \sim 30$, based on all three ^{13}C species, which they noted have similar abundances. In addition, Belloche et al. (2016) found $^{12}\text{C}/^{13}\text{C} \sim 30$ for the Sgr B2(N2) core, using ALMA data obtained for all three species. In our study, the $\text{CH}_3^{13}\text{CH}_2\text{CN}$ and $\text{CH}_3\text{CH}_2^{13}\text{CN}$ data suggested ratios near 30, but $^{13}\text{CH}_3\text{CH}_2\text{CN}$ indicated $^{12}\text{C}/^{13}\text{C} \sim 20$, reflected in both velocity components, one of which is from Sgr B2(N2). However, these differences lie within the estimated uncertainties of the ratios.

4. Discussion

4.1. A Revised $^{12}\text{C}/^{13}\text{C}$ Galactic Gradient

Based on 4 different molecules, 7 varying isotopologue combinations, and 2 separate gas components, 14 individual estimates of the $^{12}\text{C}/^{13}\text{C}$ ratio in the Galactic Center have been obtained. The average carbon isotope ratio based on these data was found to be $^{12}\text{C}/^{13}\text{C} \sim 24 \pm 9$ for the 64 km s^{-1} component and 23 ± 6 for the 73 km s^{-1} feature, see Table 3. The values for the two components are identical within the uncertainties, and there is no quantitative deviation with molecule choice. Previous estimates of the gradient in the Sgr B2 region were based on ratios obtained from CO, H_2CO , and CN ($^{12}\text{C}/^{13}\text{C} \sim 24 \pm 1, 10, >18$; see Milam et al. 2005). These new measurements, as well as others described in the Introduction, provide additional constraints for the ratio in the Galactic center.

With these new values, coupled with the CO and CN data from Milam et al. (2005), a revised Galactic gradient can be computed. (The value of $^{12}\text{C}/^{13}\text{C} = 10$ for H_2CO in Sgr B2(OH) was excluded since it is most likely optically thick). A least-squares fit to this combined data set yields

$$^{12}\text{C}/^{13}\text{C} = 5.21(0.52)D_{\text{GC}} + 22.6(3.3). \quad (1)$$

In comparison, Milam et al. (2005) calculated $^{12}\text{C}/^{13}\text{C} = 6.21(1.00)D_{\text{GC}} + 18.71(7.37)$. The new gradient therefore has a slightly shallower slope, but higher precision. A graph of the $^{12}\text{C}/^{13}\text{C}$ ratio as a function of distance from the Galactic center D_{gc} is shown in Figure 2. The newly measured $^{12}\text{C}/^{13}\text{C}$ ratios also reinforce the existence of the isotope gradient itself.

4.2. Chemical Implications for Isotopic Enrichment

This work determined column densities of various ^{13}C isotopomers of methyl acetylene ($^{13}\text{CH}_3\text{CCH}$, and $\text{CH}_3\text{C}^{13}\text{CH}$), vinyl cyanide ($^{13}\text{CH}_2\text{CHCN}$, $\text{CH}_2^{13}\text{CHCN}$, and $\text{CH}_2\text{CH}^{13}\text{CN}$), and ethyl cyanide ($^{13}\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3^{13}\text{CH}_2\text{CN}$, and $\text{CH}_3\text{CH}_2^{13}\text{CN}$), based on a wide range of transitions. Within the uncertainties, the resulting column densities and therefore abundances of the corresponding isotopologues for each of these three species were found to be the same, independent of the location of the ^{13}C substitution. This result indicates rather clearly that the formation

cyanide is the neutral-neutral reaction between ethene and the CN radical; see the scheme in Figure 3 (KIDA database: Wakelam et al. 2015: <http://kida.obs.u-bordeaux1.fr>):

This reaction has a maximum rate near 50 K of $k_9 \approx 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which diminishes by a factor of 2 approaching 300 K (Sims et al. 1993; Wakelam et al. 2015). The carbon-13 isotope could then be incorporated into vinyl cyanide via the following reactions:

For $\text{CH}_2\text{CH}^{13}\text{CN}$ to have a comparable $^{12}\text{C}/^{13}\text{C}$ ratio to $^{13}\text{CH}_2\text{CHCN}$ and $\text{CH}_2^{13}\text{CHCN}$ in this scheme, the ratios in CH_2CH_2 and CN must be very similar. Carbon-13 cannot be easily substituted on ethene, but must arise from its precursors, $\text{CH}_4 + \text{CH}$. Therefore, CH_4 , CH , and CN must all have similar isotopic compositions. Once again, it is difficult to extract the degree of ^{13}C enrichment in these molecules from the survey; CN in Sgr B2(N) shows self-absorption, CH_4 lacks a dipole moment, and CH has spectra in the submillimeter ($\nu > 300 \text{ GHz}$). Based on past observations of CN by Milam et al. (2005), however, $^{12}\text{C}/^{13}\text{C} \geq 18$ toward nearby Sgr B2(OH), consistent with the proposed scenario.

Formation on dust grains provides another synthetic route. Vinyl cyanide is created by successive hydrogenation of C_3N or HC_3N on grain surfaces, in analogy to ethyl cyanide (Caselli et al. 1993). Again, the ^{13}C distribution in the carbon backbone of vinyl cyanide therefore arises from gas-phase molecules, as for ethyl cyanide.

In contrast to vinyl cyanide, there are multiple gas-phase pathways to form CH_3CCH , as displayed in Figure 3. Hickson et al. (2016) suggest that the most likely gas-phase route to this molecule is dissociative electron recombination from protonated methylacetylene (allyl cation), $\text{CH}_2\text{CHCH}_2^+$. This reaction occurs at a rate of $\sim 3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ between 50 and 100 K (Wakelam et al. 2015). There are multiple ion-molecule routes to synthesize $\text{CH}_2\text{CHCH}_2^+$ from ethane, ethene, methane, or methyl cyanide, involving CH_3^+ , C_2H_3^+ , or C_2H_5^+ (Figure 3). These reactions all form carbon-carbon bonds, and have relatively fast rates ranging from 2.2×10^{-10} to $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Wakelam et al. 2015; Hickson et al. 2016). Two neutral-neutral reactions involving ethene or ethyl radical are also possible pathways, although the branching ratios are not certain (Hickson et al. 2016):

The rate for reaction 13 is $k_{13} \approx 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ between 50 and 100 K, while reaction 14 proceeds with $k_{14} \approx 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Canosa et al. 1997; McElroy et al. 2012).

Methylacetylene could also be produced on the surface of dust grains by sequential hydrogenation of C_3 . Again, C_3 is first formed in the gas phase, freezing in the ^{13}C tagging, and is subsequently incorporated onto grain surfaces (Hickson et al. 2016). This mechanism, however, could be disrupted by the presence of atomic oxygen on the grain surface. It is clear that there are a sufficient numbers of routes leading to the

incorporation of carbon-13 into CH_3CCH to dilute any site specificity from a given precursor.

5. Conclusion

Observations from the broadband ARO spectral-line survey of Sgr B2(N) have produced a unique data set for the ^{12}C and ^{13}C isotopologues of H_2CS , CH_3CCH , NH_2CHO , CH_2CHCN , and $\text{CH}_3\text{CH}_2\text{CN}$. The $^{12}\text{C}/^{13}\text{C}$ ratios for this cloud obtained from these molecules, involving many isotopic combinations, are nearly identical within experimental uncertainties, with the average value of 24 ± 7 . Given the varied formation pathways leading to these five species and their multiple carbon sites, such uniformity in the ratio suggests that chemical fractionation is insignificant. Therefore, the $^{12}\text{C}/^{13}\text{C}$ ratios obtained must principally reflect stellar nucleosynthesis and subsequent Galactic chemical evolution. The elevated temperatures in Sgr B2(N) effectively erase chemical fractionation effects in smaller precursor molecules, and the resulting $^{12}\text{C}/^{13}\text{C}$ ratio is then “locked” into product species. This work also suggests that measurements of the $^{12}\text{C}/^{13}\text{C}$ ratio in warmer clouds across the Galaxy are a reliable measure of the degree of GCE.

We thank the staff of ARO for making these observations possible. This research was supported by NSF grants AST-1515568 and AST-1140030. The Kitt Peak 12 m and the SMT are operated by the Arizona Radio Observatory (ARO), with partial support through the NSF University Radio Observatories (URO) program (AST-1140030). The work was also supported by NASA under Agreement No. NNX15AD94G issued through the Science Mission Directorate interdivisional initiative Nexus for Exoplanet System Science (NExSS).

ORCID iDs

D. T. Halfen <https://orcid.org/0000-0003-2483-3616>

References

- Anicich, J. 1993, *JPCRD*, **22**, 1469
- Araki, M., Takano, S., Sakai, N., et al. 2016, *ApJ*, **833**, 291
- Baskakov, O. I., Dyubko, S. F., Ilyushin, V. V., et al. 1996, *JMoSp*, **179**, 94
- Belloche, A., Müller, H. S. P., Garrod, R. T., & Menten, K. M. 2016, *A&A*, **587**, A91
- Belloche, A., Müller, H. S. P., Menten, K. M., Schilke, P., & Comito, C. 2013, *A&A*, **559**, A47
- Brauer, C. S., Pearson, J. C., Drouin, B. J., & Yu, S. 2009, *ApJS*, **184**, 133
- Canosa, A., Sims, I. R., Travers, D., Smith, I. W. M., & Rowe, B. R. 1997, *A&A*, **323**, 644
- Caselli, P., Hasegawa, T. I., & Herbst, E. 1993, *ApJ*, **408**, 548
- Cazzoli, G., & Kiesel, Z. 1988, *JMoSp*, **130**, 303
- Chiappini, C., & Matteucci, F. 2001, in AIP Conf. Proc. 598 Solar and Galactic Composition, ed. R. F. Wimmer-Schweingruber (San Francisco, CA: ASP), 227
- Colmont, J. M., Wlodarczak, G., Priem, D., et al. 1997, *JMoSp*, **181**, 330
- Dubrule, A., Boucher, D., Burie, J., & Demaison, J. 1978, *JMoSp*, **72**, 158
- Endres, C. P., Schlemmer, S., Schilke, P., Stutzki, J., & Müller, H. S. P. 2016, *JMoSp*, **327**, 95
- Esplughes, G. B., Cernicharo, J., Viti, S., et al. 2013, *A&A*, **559**, A51
- Fukuyama, Y., Odashima, H., Takagi, K., & Tsunekawa, S. 1996, *ApJS*, **104**, 329
- Gardner, F. F., & Whiteoak, J. B. 1979, *MNRAS*, **188**, 331
- Gerry, M. C. L., & Winnewisser, G. 1973, *JMoSp*, **48**, 1
- Henkel, C., Wilson, T. L., Walmsley, C. M., & Pauls, T. 1983, *A&A*, **127**, 388
- Herbst, E. 1985, *ApJ*, **291**, 226
- Herwig, F. 2005, *ARA&A*, **43**, 435
- Hickson, K. M., Wakelam, V., & Loison, J.-C. 2016, *Mol. Astrophys.*, **3**, 1
- Jones, P. A., Burton, M. G., Cunningham, M. R., et al. 2008, *MNRAS*, **386**, 117
- Langer, W. D., & Penzias, A. A. 1990, *ApJ*, **357**, 477

- Loison, J.-C., Wakelam, V., & Hickson, K. M. 2014, *MNRAS*, **443**, 398
- Maeda, A., Medvedev, I. R., Winniewisser, M., et al. 2008, *ApJS*, **176**, 543
- Margulès, L., Belloche, A., Müller, H. S. P., et al. 2016, *A&A*, **590**, A93
- McElroy, D., Walsh, C., Markwick, A. J., et al. 2012, *A&A*, **550**, A36
- Milam, S. N., Savage, C., Brewster, M. A., Ziurys, L. M., & Wyckoff, S. 2005, *ApJ*, **634**, 1126
- Motiyenko, R. A., Tercero, B., Cernicharo, J., & Margulès, L. 2012, *A&A*, **548**, A71
- Müller, H. S. P., Belloche, A., Menten, K. M., Comito, C., & Schilke, P. 2008, *JMoSp*, **251**, 319
- Müller, H. S. P., Belloche, A., Xu, L.-H., et al. 2016, *A&A*, **587**, A92
- Pagel, B. 1997, *Nucleosynthesis and Chemical Evolution of Galaxies* (Cambridge: Cambridge Univ. Press)
- Penzias, A. A. 1980, *Sci*, **208**, 663
- Pickett, H. M., Poynter, R. L., Cohen, E. A., et al. 1998, *JQSRT*, **60**, 883
- Prantzos, N., Aubert, O., & Audouze, J. 1996, *A&A*, **309**, 760
- Richard, C., Margulès, L., Motiyenko, R. A., & Guillemin, J.-C. 2013, *A&A*, **543**, 135
- Ritchey, A. M., Federman, S. R., & Lambert, D. L. 2011, *ApJ*, **728**, 36
- Sakai, N., Takano, S., Sakai, T., et al. 2013, *JPCA*, **117**, 9831
- Schmiedke, A., Schilke, P., Möller, Th., et al. 2016, *A&A*, **588**, A143
- Sims, I. R., Queffelec, J. L., Travers, D., et al. 1993, *CPL*, **211**, 461
- Timmes, F. X., Woosley, S. E., & Weaver, T. A. 1995, *ApJS*, **98**, 617
- Vasyunin, A. I., & Herbst, E. 2013, *ApJ*, **769**, 34
- Wakelam, V., Loison, J.-C., Herbst, E., et al. 2015, *ApJS*, **217**, 20
- Wilson, T. L., & Rood, R. T. 1994, *ARA&A*, **32**, 191