1. INTRODUCTION

Observations of isotopically substituted versions of interstellar molecules, their so-called isotopologues, have become the usual way of deducing atomic isotopic abundance ratios for common products of stellar nucleosynthesis—C, N, O, S, Si, Cl, etc., in the interstellar medium (ISM), as summarized by Wannier (1980) and Wilson (1999). However, the relative abundances of particular isotopologues can differ from those inherent in the gas at large owing to peculiarities of their chemistry (Watson et al. 1976; Watson 1977; Langer et al. 1984), and recognizing or explaining anomalous isotopologic abundance ratios is an ongoing challenge for astrochemistry.

The most commonly observed example of this phenomenon is with CO in diffuse clouds, where the CO/¹³CO ratio may be larger or smaller than the inherent C/¹³C ratio in the ambient gas depending on whether selective photodissociation (Bally & Langer 1982) or chemical fractionation (Watson et al. 1976) dominates (Wilson et al. 1992; Liszt & Lucas 1998; Sonnentrucker et al. 2007; Burgh et al. 2007; Sheffer et al. 2008; Liszt 2007; Visser et al. 2009). Selective photodissociation (increasing CO/¹³CO) occurs in gas seen toward a few hot stars while chemical fractionation (behaving oppositely) is a more general phenomenon that is enhanced at somewhat higher CO column densities. Chemical fractionation is also now seen in the envelopes of dark clouds (Goldsmith et al. 2008).

Gas-phase molecular cloud chemistry actually makes a rather general prediction about isotopologic abundances in strongly shielded regions: CO and molecules that form directly from it (HCO⁺, H₂CO, and CH₃OH) should show a common C/¹³C ratio that reflects the composition of the gas reservoir, while other species that form from the pool of free carbon outside CO should be strongly depleted in ¹³C (Watson 1977; Liszt 1978; Langer et al. 1984). This occurs because CO is the repository of the overwhelming majority of the gas-phase carbon and carbon is liberated from CO mainly as the dissociation product of destruction of CO by a small quantity of cosmic-ray-ionized He⁺ (i.e., He⁺ + CO → C⁺ + O + He). The resulting C⁺ ions quickly interact with the ambient CO, and the fact that ¹³CO is more strongly bound than ¹²CO results in a preferential deposition of ¹³C into ¹³CO through the reaction ¹³C⁺ + ¹²CO → ¹²C⁺ + ¹³CO + 34.8 K (Watson et al. 1976, see Appendix A here). In this way ¹³C⁺ preferentially disappears from the pool of C⁺ and from the general pool of carbon available to form most species. The C⁺/¹³C⁺ ratio increases by a factor approaching exp(34.8/TK) but the CO/¹³CO ratio changes little because the C⁺/CO abundance ratio is so small, below 10⁻³.

It quickly became apparent that there was some tension between this prediction and observations of interstellar gas showing C⁺/¹³C ratios that were, if anything, below the terrestrial value of C/¹³C = 89. Now, it is acknowledged that the local interstellar carbon isotope ratio is in the range 60–70, but at the time, Watson (1977) suggested a mechanism involving selective depletion of carbon onto grains, offering the possibility of lowering the C/¹³C ratio. Detailed time-dependent models showed very complex behavior in the isotopologic ratios but largely failed to bear out this suggestion (Liszt 1978), finding that ¹³C enhancement outside CO only occurred as molecules disappeared from the gas.

Because of the possibility of fractionation in fully molecular gas, some observers changed the focus of their work to concentrate on measurement of carbon isotope ratios using only the isotopologues of carbon monoxide (Langer & Penzias 1993), but it seems fair to say that anomalously large C/¹³C ratios have never been seen in the molecular cloud HII regions that are typically used for isotope determinations (Wannier 1980; Wilson 1999). Indeed, a recent survey of the carbon isotope ratio in CN does not seem to have been affected (Milam et al. 2005) and Tercero et al. (2010) report C/¹³C = 45 ± 20, S/³⁴S = 20 ± 6 from a survey of sulfur-bearing carbon chain molecules in Ori KL. Fractionation effects may be minimized at the somewhat higher temperatures of clouds near HII regions but are not entirely eliminated. The absence of observable effects from the
predicted carbon fractionation chemistry has been a lingering, if not entirely obvious, mystery.

By contrast, anomalies of two kinds have now been noted in cold gas in/near the cyanopolyne peak in the Taurus molecular cloud (TMC) for species containing several carbon atoms, and Sakai et al. (2007, 2010) appealed to the work of Langer et al. (1984) for an explanation. $^{13}$C is strongly but very unequally lacking in both of the singly substituted $^{13}$C isotopologues of CCH (Sakai et al. 2010) and is deficient in $^{13}$CCS but not $^{13}$CS. A small effect may also be present in HC$_3$N in Taurus

| Species          | Frequency (MHz) | Cyan Peak (K km s$^{-1}$) | L1527 (K km s$^{-1}$) | NH$_3$ Peak (K km s$^{-1}$) |
|------------------|-----------------|---------------------------|------------------------|-----------------------------|
| HNC              | 90663.56        | 1.597 (0.020)             | 1.850 (0.040)          | 2.550 (0.020)               |
| $^{13}$HNC       | 87090.85        | 0.551 (0.023)             | 0.263 (0.022)          | 0.650 (0.026)               |
| $^{13}$H$_2$CS   | 88656.69        | 0.120 (0.016)             | 0.055 (0.015)          | 0.086 (0.016)               |
| CS               | 97980.95        | 0.980 (0.011)             | 1.495 (0.023)          | 1.685 (0.010)               |
| $^{34}$S         | 96412.95        | 0.362 (0.014)             | 0.116 (0.009)          | 0.341 (0.005)               |
| $^{13}$CS        | 92949.27        | 0.121 (0.008)             | 0.045 (0.007)          | 0.100 (0.008)               |
| H$_2$CS          | 103040.28       | 0.483 (0.012)             | 0.102 (0.019)          | 0.272 (0.011)               |
| H$_2$C$_3$S      | 101284.40       | 0.0218 (0.0044)           |                        |                            |
| $^{13}$H$_2$CS   | 99077.84        | 0.0063 (0.0016)           |                        |                            |

Notes.

a For entries $\int T^2 dv$ quantities in parentheses are 1σ uncertainty.
b For details of the H$^{13}$C spectrum see van der Tak et al. (2009).

c The main isotopologues of HNC and CS are optically thick in the foreground envelopes; it is not possible to measure the C$^{15}$N ratio in the C$_3$S line.
d For N(HNC)/N(H$^{13}$NC) = 250–330 and $\tau = 0$ in the H$^{13}$C line.
e For N(HNC)/N(H$^{15}$NC) = 250–330 and $\tau = 0.6$ in the H$^{13}$C line.
f For N(C$^{13}$S)/N(C$^{15}$S) = 22.7 and $\tau = 0$ in the C$^{13}$C line.
g For N(H$_2$CS)/N(H$_2$C$^{13}$S) = 22.7 and $\tau = 0$ in the H$_2$C$^{15}$S line.

ARO 12 m, $T_R^* \approx 0.85$ $T_{mb}$. Line frequencies were taken from the online splotalog (http://www.splotalogue.net) and are given in Table 1 representing the new results.

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3. OBSERVATIONAL RESULTS

3.1. New Results

Spectra are shown in Figure 1 and numerical results are summarized in Table 1 giving profile integrals and Table 2 giving ratios of line profile integrals and implied carbon isotope ratios, assuming values for N/$^{13}$N or S/$^{34}$S as indicated.

The main isotopologues of HNC and CS are optically thick and self-absorbed by weakly excited molecules within the foreground envelopes; it is not possible to measure the C$^{15}$C ratios in these species directly, and we must assume values for the isotopic ratios in sulfur and nitrogen. For nitrogen the interstellar N$^{15}$N ratio is now seen to be only slightly larger than the terrestrial value of 270. Lis et al. (2010) found N$^{15}$N = 334 ± 50 (3σ) toward Barnard 1, and Adande & Ziurys (2012) find N$^{15}$N = 290 ± 40 at the solar circle from a large-scale galactic survey of CN emission. In local diffuse clouds, Lucas & Liszt (1998) found N$^{15}$N = 240 ± 25. The range of values implied for HNC/H$^{13}$C in Table 2 corresponds to HNC/H$^{15}$NC = 250–330 and the statistical uncertainties are quoted at each end of the range.

No systematic deviations from the solar system value of S/$^{34}$S = 22.7 have been seen in specific isotope studies of the local ISM (Wannier 1980; Wilson 1999; Tercero et al. 2010) and the implied values of CS/$^{13}$CS quoted in Table 2 correspond to this value and the statistical uncertainties of the current measurements. Our measurements of H$_2$CS isotopologues toward TMC1 are in accord with this. Some uncertainty accrues from the unmeasured optical depth of the rarer isotopologues as discussed in the following subsection.

The result for the isotopic carbon ratio in H$_2$CS is of marginal significance and will not be discussed further, but it seems clear from Table 2 that there is no strong depletion of $^{13}$C in HNC or CS.

| Species          | Cyano Peak (MHz) | L1527 (K km s$^{-1}$) | NH$_3$ Peak (K km s$^{-1}$) |
|------------------|------------------|------------------------|-----------------------------|
| W(H$^{13}$C)/W(H$^{15}$NC) | 4.59 (0.64)       | 4.78 (1.36)            | 7.56 (1.44)                 |
| N(HNC)/N(H$^{13}$C) | 54.8–72 (10)      | 52 (15)–69 (20)        | 33 (6)–44 (8)               |
| N(HNC)/N(H$^{15}$C) | 43 (6)–57 (9)     |                        |                            |
| W($^{13}$CS)/W(C$^{14}$S) | 0.334 (0.024)     | 0.385 (0.066)          | 0.293 (0.028)               |
| N(C$^{13}$S)/N$^{15}$CS | 68 (5)            | 59 (10)                | 77 (7)                      |
| N(C$^{13}$S)/N$^{15}$CS | 71 (5)            |                        |                            |
| W(H$_2$CS)/W(H$_2$C$^{13}$S) | 22.9 (4.2)        |                        |                            |
| W(H$_2$C$_3$S)/W(H$_2$C$^{15}$S) | 0.289 (0.094)     |                        |                            |
| N(H$_2$CS)/N(H$_2$C$^{13}$S) | 79 (26)           |                        |                            |
3.2. Correction for Finite Optical Depth

3.2.1. CS

The presence of a finite optical depth in the C$^{34}$S line would cause compression of the $W(C^{34}S)/W(^{13}CS)$ intensity ratio, resulting in an underestimate of the $N(C^{34}S)/N(^{13}CS)$ and $N(CS)/N(^{13}CS)$ column density ratios. For TMC1, Pratap et al. (1997) derived $N(C^{34}S) = 2.0 \times 10^{12}$ cm$^{-2}$, consistent with an estimate $N(C^{34}S) = N(CS)/22.7 = 5 \times 10^{13}$ cm$^{-2}/22.7 = 2.2 \times 10^{12}$ cm$^{-2}$ from the work of Ohashi et al. (1992). For $N(C^{34}S) = 2.0 \times 10^{12}$ cm$^{-2}$ and peak line brightness of 0.72–0.85 K, depending on beam efficiency, we calculate that the central optical depth of the C$^{34}$S $J = 2$–1 line toward TMC1 must be below 0.15 and the excitation temperature in the lower part of the rotation ladder must be fairly high, above about 8 K for $J = 2$–1, based on modeling of the excitation. In this case the $^{13}$CS line is quite optically thin and the observed isotopolog ratio is at most 5% below the intrinsic abundance ratio. Accordingly, the entry corrected for optical depth in Table 2 is the uncorrected value increased by 5%.

Estimates of the optical depth correction toward the other pointing positions do not seem possible. Toward the NH$_3$ peak, Pratap et al. (1997) derived a higher column density $N(C^{34}S) = 4.3 \times 10^{12}$ cm$^{-2}$ while the observed line in this work is only slightly broader and noticeably less bright. Excitation solutions for such high column density in the face of relatively weak emission indicate high optical depth at lower excitation temperatures (5 K) that do not seem consistent with the physical conditions toward the NH$_3$ peak, that are not less dense or colder than toward TMC1. Pratap et al. (1997) cited problems with their modeling of the CS lines, such that they were compelled to use a very small isotopolog abundance ratio CS/$C^{34}$S = 12–14. Although they cited a reference to the isotopic composition of cosmic rays in defense of this assumption, it is without precedent in molecular gas and would lead to improbably small values of the CS/$^{13}$CS ratio if used in this work. We conclude that we...
Table 3
Other Measured and Inferred $^{12}$C/$^{13}$C Ratios\(^a\)

| Species | Cyano Peak | 1521E | L1527 | NH\(_3\) | Ref. |
|---------|------------|-------|-------|---------|-----|
| CCH/\(^{13}\)CCH | >250\(^b\) | >135\(^c\) | 2 | 1 |
| CCH/\(^{13}\)CH | >170\(^b\) | >80\(^c\) | 2 |
| CCS/\(^{12}\)CCH | 230(43) | >130 | 2 |
| C\(^{13}\)S/\(^{12}\)CCS | 54(2) | 51(4) | 2 |
| C\(^{13}\)S/\(^{13}\)CCS | >191 | >107 | 2 |
| HC\(_3\)N/H\(^{13}\)CCN | 79(11) | | 3 |
| HC\(_3\)N/H\(^{13}\)CCN | 75(10) | | 3 |
| HC\(_3\)N/H\(^{13}\)CCN | 55(7) | | 3 |

Notes.
\(^a\) Lower limits are 3σ; rms in parentheses are 1σ.
\(^b\) \(^{13}\)CCH/\(^{13}\)CCH = 1.6 ± 0.4(0/3/0).
\(^c\) \(^{13}\)CH/\(^{13}\)CH = 1.6 ± 0.1(3/0).

References. (1) Sakai et al. 2010; (2) Sakai et al. 2007; (3) Takano et al. 1998.

cannot make a reliable correction for optical depth correction except toward TMC1 where all indications are that the opacities in the rarer CS isotopologues are small.

3.2.2. HNC

For HNC, the \(^{13}\)C-bearing isotopologue is the more abundant of the two variants used to derive the C/\(^{13}\)C ratio, so the effect of optical depth is opposite to that in the case of CS: the derived HNC/HN\(^{13}\)C ratio decreases with increasing optical depth in the rare isotopologues. Indeed, the optical depths encountered in HNC are higher than for CS and the correction for finite optical depth is rather larger. Unfortunately, we did not resolve the hyperfine structure of HN\(^{13}\)C and cannot duplicate the excitation temperature-opacity derivation of Padovani et al. (2011) who observed at other positions in Taurus having higher optical depth than occurs toward TMC1.

Pratap et al. (1997) gave $\lambda$(HN\(^{13}\)C) = 4.2 × 10\(^{-12}\) cm\(^{-2}\) toward TMC1 while a slightly smaller upper limit $\lambda$(HN\(^{13}\)C) < 2 × 10\(^{-14}\) cm\(^{-2}\)/60 < 3.3 × 10\(^{-12}\) cm\(^{-2}\) can be inferred from the tabulation of Ohishi et al. (1992). For the comparatively weak emission lines we observed, these column densities imply $J$ = 1–0 excitation temperatures around 4 K and optical depths of order two in HN\(^{13}\)C, so that even such a rare isotopologue would be somewhat self-absorbed. With optical depths this large, simply requiring that HNC/HN\(^{13}\)C be above 60 limits the possible range of assumed values for $\lambda$(HNC)/$\lambda$(HN\(^{13}\)C) to be nearer the large end of the likely range. However, the small excitation temperatures implied by our observed brightnesses and the higher of the previously measured column densities are not consistent with the densities that are inferred for the Taurus cores, which imply higher excitation temperatures, lower optical depths, and smaller column densities.

We conclude that it is not possible to derive an entirely accurate carbon isotopologue ratio in HNC based on correcting the observed intensity ratios for optical depth but the errors do go in a known direction. Table 2 shows a range of carbon isotope ratios derived from HNC for an optical depth 0.6 in the HN\(^{13}\)C line toward TMC1, corresponding to an excitation solution with $\lambda$(HN\(^{13}\)C) = 2 × 10\(^{-13}\) cm\(^{-2}\) that is consistent with the work of Ohishi et al. (1992). This could still underestimate the optical depths and so overestimate the C/\(^{13}\)C ratio.

3.3. Previously Reported \(^{13}\)C Anomalies

These are summarized in Table 3 where all the results are cast in terms of actual or implied C/\(^{13}\)C ratios, using the terrestrial sulfur isotopic ratio as appropriate. There are two effects that must be considered: \(^{13}\)C is strongly lacking in some isotopologues but to different degrees depending upon placement. Thus, both CCH and C\(^{13}\)CH are underabundant but more so in the former (a factor 1.6) and in CCS only the more tightly bound isotopologue \(^{13}\)CCS exhibits the effect; in each case, the isotopologue with an inboard \(^{13}\)C is more abundant. In C\(_3\)S only \(^{13}\)CCCS was observed, but is heavily deficient. In terms of chemical models these two considerations are separately reflected in, on the one hand, the overall C/\(^{13}\)C ratio in the gas, and, on the other, the detailed path to formation (and perhaps in situ fractionation after formation) of the individual species studied.

Sakai et al. (2007, 2010) discussed in exquisite detail the formation routes to CCS and CCH, concluding that the unequal depletions of the \(^{13}\)C-bearing isotopologues were the result of formation reactions in which the carbon atoms were not equivalent (for CCH, C + CH\(_2\) → CCH + H and not C\(_2\)H\(_2\) + e → CCH + H\(_2\)) rather than alterations that might have occurred after formation (for instance \(^{13}\)CCH + H → C\(^{13}\)C + H + 8.1 K or \(^{13}\)CCS + S → C\(^{13}\)CS + S + 15 K). They also concluded that they had confirmed observationally the phenomena modeled by Langer et al. (1984) whereby the relatively famous fractionation reaction involving CO and \(^{13}\)C induces a very general vanishing of \(^{13}\)C from the gas at large as discussed in the Introduction here.

4. CARBON ISOTOPIC AND ISOTOPOLOGIC RATIOS IN THE TAURUS CORES

The C/\(^{13}\)C ratios inferred from our work are consistent with other measurements of the carbon isotopic ratio in the nearby ISM that find C/\(^{13}\)C = 60–70 and show no sign of the \(^{13}\)C depletion that is predicted for the gas-phase chemistry. The CS isotopologues we observed would not serve as the basis for substantially depleted CCS but are instead close to the CCS/C\(^{13}\)CS ratio 54±2 discussed by Sakai et al. (2007), suggesting that CCS could indeed form directly through a reaction like CH + CS → CCS + H as hypothesized by Sakai et al. (2007).

In fact, Furuya et al. (2011) recently reached something of the same conclusion through chemical modeling, without the new observational result for CS. They considered a time-dependent model for TMC1 with all the carbon initially in the form of C\(^{13}\) (see Liszt 2009), in which the abundance of CO is relatively small even when it begins to deplete out of the gas onto grains; the CO column in their model is also rather small compared with N(CO) = 500 N(C\(^{15}\)O) = 1.8 × 10\(^{15}\) cm\(^{-2}\) from Pratap et al. (1997). Because of the assumed initial conditions, a very large portion of the gas-phase carbon remains outside CO, and, for reasons that are discussed in Section 5, \(^{13}\)C depletion in the gas as a whole is generally modest. C/\(^{13}\)C is typically of order 110 after the earliest times. In this case the hypothesis of a rearrangement effected by reaction of CCS and H yielded CCS/C\(^{13}\)CS = 230, CCS/C\(^{13}\)CS = 54, as observed. That is, the rare isotopologues both form with C/\(^{13}\)C = 110 but the rearranged reaction C\(^{13}\)CS + H → C\(^{13}\)CCS + C\(^{13}\)S + C\(^{13}\)H\(_2\) is strongly energetically favored at 10 K driving CCS/C\(^{13}\)CCS up while CCS/C\(^{13}\)CS falls to half the C/\(^{13}\)C ratio in the gas (110/2). Our results suggest that CCS and C\(^{13}\)S actually form with CCS/C\(^{13}\)CS and CCS/C\(^{13}\)CS ≅ 70.

Furuya et al. (2011) also showed that the known rearrangement reaction for CCH with ambient H (that has a smaller exothermicity 8 K) could yield unequal isotopolog abundances.
to the degree observed (a factor 250/170), but the relatively small amount of $^{13}$C depletion in their model did not come close to reproducing the very large individual CCH/$^{13}$CCH or CCH/$^{13}$CH ratios that are observed (170 and 250; Table 3). Even so, their model generally predicts larger values for $N$(CS)/$N$(13CS) than we observe. It is not obvious that this scheme would function as well in a gas that was even more weakly fractionated, if it caused very small values for the CCS/$^{13}$CCS ratio.

The smaller isotopologic discrepancies that are observed in HC$_3$N can likely be achieved by relatively weakly endothermic rearrangement reactions with hydrogen in an unfracated gas, consistent with the lack of fractionation we infer for HNC. In summary, the observational situation is complex and somewhat mysterious. CS, HNC, and HC$_3$N suggest that there is little fractionation in the carbon pool at large while the seeming absence of fractionation in CCS/$^{13}$CS may be accidental and the anomalies in CCH remain unexplained. Disparities among the carbon isotopologues in individual species with more than one carbon atom seem best explained by rearrangement reactions with atomic hydrogen, but the very large isotopologic ratios seen in CCH remain beyond the reach of current explanations, and the disparity that is observed in CCS may be inconsistent with rearrangement in a gas that is too lightly fractionated.

5. WHERE IS THE COSMIC-RAY IONIZATION-DRIVEN FRACTIONATION?

The possibility of a strong overall carbon fractionation in species other than CO has been recognized ever since the existence of the C$^+$ + CO fractionation reaction was first remarked. Nonetheless, it was not observed in surveys that sought to determine the carbon isotope ratio but found the same values in CO and CS and CN, etc., even though the latter species do not form from CO and could have shown strong fractionation effects even in relatively warm gas. Even now, despite the carbon isotopologic anomalies that are seen at very low temperatures (10 K) in Taurus in some polyatomics bearing more than one carbon, the gas there cannot obviously be said to be fractionated as a whole. Here we ask why this is so.

5.1. The Role of He$^+$

The prediction of strong overall fractionation arises in models of the gas-phase chemistry of dense dark oxygen-rich material (O/C > 1) where CO is by far the largest repository of gas-phase carbon atoms (Langer et al. 1984). A few molecular species form directly from CO—HCO$^+$ in the gas, H$_2$CO and CH$_3$OH from successive hydrogenation of CO on grains—and will share its C/$^{13}$C ratio. Other carbon-bearing trace molecules in the gas result from the relatively small amount of carbon that is liberated when He$^+$, ionized by cosmic rays, slices CO apart into C$^+$ and O via the reaction He$^+$ + CO $\rightarrow$ C$^+$ + O + He; the reaction rate constant is 1.6 x 10$^{-9}$ cm$^3$ s$^{-1}$ (see Table 4 for important reactions and rate constants). The only reaction competing effectively with this one for the attentions of He$^+$ is the charge-exchange ionization of H$_2$, He$^+$ + H$_2$ $\rightarrow$ H$^+$ + H$_2$, whose currently accepted reaction rate constant is 7.2 x 10$^{-15}$ cm$^3$ s$^{-1}$ (Table 4). Langer et al. (1984) included instead the reaction He$^+$ + H$_2$ $\rightarrow$ H$^+$ + H + He with the much larger rate constant 1.5 x 10$^{-13}$ cm$^3$ s$^{-1}$, which significantly dampened the effects of fractionation compared to what would be derived in more recent chemical models: that reaction is now considered to be negligibly slow in cold gas, see Table 4.

The ratio of reaction rates and abundances determines whether CO or H$_2$ controls the abundance of He$^+$ but for X(CO) > 4.5 x 10$^{-6}$, when CO dominates using currently accepted reaction rate constants, every cosmic-ray ionization of an He atom results in the production of a C$^+$ ion. Because He is so much more abundant than carbon (i.e., CO), the volume rate of production of C$^+$ ions and the rate at which carbon is liberated from CO is approximately 1000 times higher than the rate at which cosmic rays interact with CO directly; this factor is independent of the cosmic-ray ionization rate n(He$^+$) and independent of X(CO) when the reaction with CO is the main destroyer of He$^+$.

It is important to stress just how rapidly the chemical ionization of carbon occurs via He$^+$ + CO, because the only competing mechanism for liberating atomic carbon from CO is photodissociation. In quiescent, shielded, cosmic-ray-heated gas, cosmic-ray-induced photodissociation typically occurs at rates that are a much smaller multiple of the cosmic-ray ionization rate, and is some 50 times slower than He$^+$+ CO. The point is that in these models it is difficult to contrive to liberate carbon from CO except, initially, as C$^+$, leading to fractionation.

5.2. The Role of the CO + C$^+$ Fractionation Reaction

Just as He$^+$ reacts most commonly with CO, so does C$^+$, although in this case there is a wider range of competitive reactions (see Table 4). But to the extent that C$^+$ interacts with CO, it preferentially deposits $^{13}$C$^+$ back in CO. Meanwhile, the abundance of C$^+$ is so small relative to that of CO (typically

---

**Table 4**

| Reactant | Relative Abundance | $w$/He$^+$ (cm$^3$ s$^{-1}$) | $w$/C$^+$ (cm$^3$ s$^{-1}$) |
|----------|-------------------|-----------------------------|-----------------------------|
| H$_2$    | 1                 | $7.2 \times 10^{-15} + 3.7 \times 10^{-14}$ exp(−35/T$_K$) | $4.0 \times 10^{-16}$ (300/T$_K$)$^{0.20}$ |
| CO       | $8.0 \times 10^{-5}$ | $1.6 \times 10^{-9}$ | See Appendix A |
| e        | $2.4 \times 10^{-7}$ | $3.3 \times 10^{-9}$ | $7.2 \times 10^{-12}$ (300/T$_K$)$^{0.834}$ |
| M        | $3.4 \times 10^{-7}$ | $1.6 \times 10^{-9}$√(300/T$_K$) | $1.5 \times 10^{-9}$ |
| CH       | $1.0 \times 10^{-7}$ | $1.0 \times 10^{-9}$√(300/T$_K$) | $3.8 \times 10^{-10}$√(300/T$_K$) |
| OH       | $3.0 \times 10^{-7}$ | $1.0 \times 10^{-9}$√(300/T$_K$) | $7.7 \times 10^{-10}$√(300/T$_K$) |
| O$_2$    | $1.0 \times 10^{-7}$ | $1.0 \times 10^{-9}$√(300/T$_K$) | $1.0 \times 10^{-9}$√(300/T$_K$) |
| H$_2$O   | $1.0 \times 10^{-7}$ | $4.8 \times 10^{-10}$√(300/T$_K$) | $2.7 \times 10^{-10}$√(300/T$_K$) |
| N$_2$    | $1.2 \times 10^{-5}$ | $1.6 \times 10^{-9}$√(300/T$_K$) | $1.6 \times 10^{-9}$√(300/T$_K$) |

Note. * Wolfrre et al. (2008), includes dielectronic recombination.
less than 0.1\%) that any effect on the isotopolog abundance ratio in CO is imperceptible. The final result is that when free atomic carbon is primarily liberated and maintained in the form of C^+, the pool of gas-phase carbon outside CO inevitably becomes depleted in ^13C, hence in ^13C, as long as CO remains sufficiently abundant in the gas to dominate the neutralization of He^+. CO and the free carbon pool coexist but with two distinct C/^13C ratios that are separately passed on to their descendant molecules.

5.3. So Indeed, Why Is a More General ^13C Depletion Not Seen in Taurus?

To blunt the effect of C^+ fractionation it is necessary to interfere with the C^+-CO interaction and there are various choices for doing so, for instance, (1) a low CO abundance, such as might occur at later times after depletino onto dust (see also the early-time model of Furuya et al. (2011) in which CO never attains its full abundance); (2) very large abundances of species like OH and O_2 that react rapidly with C^+; (3) taking the high-metals case where sulfur and silicon are not assumed to be strongly depleted from the gas so that they dominate the neutralization of C^+ through charge exchange; (4) the presence of polycyclic aromatic hydrocarbon (Wakelam & Herbst 2008; Lepp et al. 1988) to neutralize C^+ more rapidly, although these are not always assumed to survive in dense gas. Nonetheless, fractionation at the level of a factor two or so persists in the C^+ until CO and C^+ are all but gone from the gas.

Preventing fractionation of the pool of molecules outside the small family that forms from CO really requires that the reservoir of carbon outside CO must reside mostly in the form of neutral atomic carbon with perhaps some small admixture of C^+. Given that C^0 typically reacts with neutral molecules at least 20 times more slowly than does C^+, the proportion of C^0 to C^+ should be very large and the real question is how this might come about. One possibility that is capable of maintaining very large free neutral atomic carbon fractions is the so-called high-ionization phase of bistable solutions of the chemical equilibrium equations, whose relevance has recently been discussed in terms remarkably similar to the considerations here for controlling the C^+ abundance (Charnley & Markwick 2003; Wakelam et al. 2006; Boger & Sternberg 2006). Extension of the bistability discussion to include fractionation effects is clearly of great interest.

It is generally not possible to create a sufficient pool of neutral carbon using just the in situ flux of CO-dissociating photons generated by the cosmic-ray-induced electronic excitation of H_2 (Prasad & Tarafdar 1983; Sternberg et al. 1987) because these photons dissociate CO at rates that are a relatively small multiple of the cosmic-ray ionization rate: Langer et al. (1984) assumed a multiple of 10. As such, cosmic-ray-induced photons liberate neutral atomic carbon much more slowly than CO is sliced into C^+ and O by He^+. Because the naturally arising local flux of CO photodissociating photons inside dark gas is so weak, some attempts to explain the existence of even a relatively small amount of C^0 in dense gas invoke special mechanisms such as inversion of the normal [O]/[C] > 1 ratio (Langer et al. 1984), penetration of ambient UV light into a porous, heavily clumped medium and/or recent cloud formation (Phillips & Huggins 1981), turbulent diffusion that cyclically exposes heavily shielded gas to the ambient UV radiation field near the cloud surface (Boland & de Jong 1982; Willacy et al. 2002; Xie et al. 1995), and the presence of the so-called high-ionization phase of bistable chemical reaction schemes (Flower et al. 1994).

The inference of a large pool of free atomic carbon in dense dark gas is really not an observational problem per se because substantial columns of C^0 are typically found toward and around dark clouds (Ferking et al. 1989) including toward TMC1 where N(C^0)/N(CO) η 0.1 (Maezawa et al. 1999). This is very large compared to the values X(C^+)/X(CO) ≈ 3 × 10^{-3}/8 × 10^{-5} ~ 4 × 10^{-4} that arise from the default parameters in our toy model (Appendix B). However, the observational situation is complicated by superposition of different density regimes along the line of sight and it is hard to assess how much of the observed atomic carbon actually exists inside the darkest gas. This is especially true given the recent revelation of the preponderance of low-A_V material in Taurus and other dark cloud complexes (Pineda et al. 2010; Cambresy 1999). Extrapolation of the results of Bensch et al. (2003) to much higher N(CO) suggests that perhaps 1%-2% of the carbon budget (Gerin et al. 2003) could exist as C^0 at N(CO) ~ 10^{18} cm^{-2}. This would be about 50 times more carbon than exists in C^+.

5.4. Relevance to Other Environments

The possibility of chemical fractionation in cold cores raises important questions for understanding carbon isotopic abundances in planetary and protoplanetary systems including the solar system and protosolar nebula. For example, is it correct to ascribe the difference between the solar ratio C/^13C = 89 and that in the nearby ISM (60–70) entirely to chemical enrichment since the birth of the solar system or might fractionation be responsible (Smith et al. 2011)? Why are there differences between the carbon isotope ratios measured in various comets and between those measured in comets and that in the Sun (Crovier et al. 2009; Mumma & Charnley 2011)? Other questions arise in matters involving other elements, for instance the difference between the N/^15N ratio in the Earth (270) and Sun (420) and the wide disparities in D/H measurements between that in Earth’s oceans (1.6 × 10^{-4}), the more nearly cosmological ratios seen in the outer planets (3–5 × 10^{-5}), and the much higher than telluric D/H ratios seen in most comets (Crovier et al. 2009; Mumma & Charnley 2011), although, apparently, not all (Hartogh et al. 2011).

Many of the effects discussed here occur prominently in recent models of fractionation chemistry in protoplanetary disks (Woods & Willacy 2009), which illustrate the complexity of relating isotope ratios in the protoplanetary nebula or planetary disk (when formed) to that in the ambient natal material. Fractionation varies with disk radius and disk height and evolves with time under the combined influence of the protostellar and interstellar radiation fields. Woods & Willacy (2009) conclude that solar system cometary material has been reprocessed, raising the question of whether any memory of conditions in natal molecular material persists into fully formed planetary systems.

6. SUMMARY

Since the initial recognition of the carbon isotope fractionation reaction, a conflict has existed between the very general prediction of a strong ^13C depletion in molecules other than CO and the general absence of observable effects in surveys of the C/^13C isotopic abundance ratio deduced form such common species as CS or CN. ^13C depletion is predicted to occur when carbon is liberated from CO by the reaction He^+ + CO → C^+ +...
O + He and remains in the gas as C⁺ to interact and fractionate with CO. Eventually, CO depletion onto grains will blunt the effect at late times, but in the meanwhile quite large variations in the abundances of ¹³C-bearing molecules are predicted for all species that do not form directly from CO. The point is that CO remains very nearly unfracationed as long as it is the main carbon reservoir in the gas and \(X(C^+)/X(CO)\) is very small, so that species like HCO⁺, H₂CO, and C₂H₅OH will also be unfracationed. But the relatively small pool of carbon that exists outside of CO to form other molecules than those in the CO family becomes strongly depleted in ¹³C and molecules that form from it (most carbon-bearing species) will also show strong ¹³C depletion.

However, strong anomalies in CCH and in some isotopologues of CCS and CCCS have recently been observed in cold dark gas in TMC1 and other cores in Taurus (less strongly in HC₅N there). It was suggested that the predicted fractionation effects had at long last actually been seen, albeit in only some very cold gas. We showed here that ¹³C fractionation does not occur in two species having a single carbon (CS and HNC) seen toward TMC1 in Taurus; we also observed these species toward other positions, finding certainly no clear evidence of fractionation, but derivation of an accurate isotopic abundance was frustrated by the difficulty of correcting for finite optical depth even in very rare isotopologues. In any case, our observations toward TMC1 make it unlikely that any general depletion of ¹³C exists in the gas at large outside CO and we discussed the implications of this inference in the context of the chemistry of an optically shielded dense gas with a normal ratio \([O]/[C] > 1\).

In general, preventing an overall ¹³C fractionation requires that the pool of gas-phase carbon outside CO resides in the gas mostly as C⁰ rather than C⁺. This could happen if the \([O]/[C]\) ratio is less than unity or if some mechanism is invoked to liberate neutral carbon from CO through photodissociation deep inside dark gas, but the most interesting possibility is that the TMC1 gas is in the so-called high-ionization state of a bistable chemical network. In any case, we are left with the fact that the overall carbon pool outside CO is apparently not depleted in ¹³C even if there is no way to prevent \(C^+/C^+ + C^+\text{CO} \rightarrow C^+\text{CO} + C^0\) to 60. For the chemistry this has interesting consequences; reactions involving C⁺ see a pool of carbon depleted in ¹³C while those with C⁰ do not, and the main pool of carbon is in larger amounts of C⁰ that react somewhat more slowly, with a normal \(C^0/C^+\) ratio.

In the future it may be possible to ascertain the overall composition of the carbon pool deep inside TMC1 using high spatial resolution observations of submillimeter lines of C₁ at ALMA, and perhaps even to measure the \(C^0/C^+\) ratio using the 492.164 GHz line of ¹³C that is displaced from the main isotope. In the meantime it is important to assess just which chemical species are subject to isotopolog abundance anomalies—apparently, a wide variety of tri- and polyatomics hosting more than one carbon atom—and under what conditions they arise, and to avoid using strongly affected molecules to derive isotopic abundance ratios.

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APPENDIX A

THE FRACTIONATION REACTION

Smith & Adams (1980) did not give analytic forms for their measurements of the temperature dependence of the carbon fractionation reaction first cited by Watson et al. (1976). Liszt (2007) provided the expressions

\[
k_f = 7.64 \times 10^{-9} T_k^{-0.55} \text{cm}^3 \text{s}^{-1} (T_k = 80–500 \text{K})
\]

\[
k_f = \frac{1.39 \times 10^{-9} T_k^{-0.05}}{1 + \exp \left( -34.8/T_k \right)} (T_k = 10–80 \text{K})
\]

for the forward (exoergic) and reverse reaction rates \(k_f\) and \(k_r\).

APPENDIX B

A TOY MODEL OF ¹³C DEPLETION

We constructed a formal model of the chemistry in which C⁺ is produced by the action of He⁺ on a fixed abundance of CO \((x(CO) = n(CO)/n(H_2) = 1)\) and solved for the densities \(n(¹³C^+), n(¹³C^+),\) and \(n(He^+)\). In addition to the fractionation reaction with CO, C⁺ is destroyed by interaction with H₂, hydrides (CH, NH, OH), O₂, thermal electrons, and charge exchange with a single low-ionization metal species denoted “M” and given the atomic properties of silicon. For the reactions in Table 4, we used the dipole-enhanced rates given on the UFDA06 database Web site http://www.ufda.net

(Woodall et al. 2007).

The default values of the reactant abundances are given in Table 4 and quoted in Figure 2, i.e., \(n(H_2) = 10^4 \text{cm}^{-3}, T_k = 10 \text{K}, \zeta_{H_2} = 2 \times 10^{-17} \text{s}^{-1}\). For the default electron abundance \(2.4 \times 10^{-7}\) we used the expression in Oppenheimer & Dalgarno (1974); alternatively see McKee (1989). The default carbon isotopic ratio is \(R_{12/13} = [¹²C]/[¹³C] = 60\). The entry for “M” represents all heavy atoms with ionization potentials less than 10 eV or so and the default is for strong depletion—the typical “low metals” case. Nitrogen was assumed to exist in the form of N₂ with a solar \([N]/[C]\) ratio and carbon depletion in the model corresponds to the default value \(x(CO) = 8 \times 10^{-5}\).

For He⁺

\[
dn(He^+)/dt = \zeta_{He} n(He) - n(He^+) n(H_2) \sum_j k_j X_j,
\]

where the fractional abundances of the reactants \(j\) are \(X_j\) and their reaction rate constants with He⁺ are \(k_j\) (listed in Table 4). For He, we take the local galactic disk abundance \([He]/[H] = 0.088\) (Balser 2006). The cosmic-ray ionization rate of He is \(\zeta_{He} = 1.08 \zeta_{H_2}/2\) and \(\zeta_{H_2} = 2 \times 10^{-17} \text{s}^{-1}\). In general, direct recombination of atomic ions with ambient electrons is utterly insignificant in this context.
Figure 2. Toy model of the $^{13}$C+, $^{12}$C+ chemistry. In each panel the solid line is $X(\text{C}^+)$, the (red) dashed line is $[^{12}\text{C}]/[^{13}\text{C}] \times X(\text{CO})/X(\text{CO})$ and the (blue) dotted line is $X(\text{He}^+)$ (only shown in some panels). Standard values are $T_K = 10\ K$, $n(\text{H}_2) = 10^4\ \text{cm}^{-3}$, $\zeta = 2 \times 10^{-17}\ \text{per H}_2$, $X(\text{CO}) = 8 \times 10^{-5}$, $X(\text{M}) = 3 \times 10^{-7}$, $X(\text{O}_2) = 3 \times 10^{-7}$, and $^{12}\text{C}/^{13}\text{C} = 60$. The panels of this figure show the effects of varying individual parameters. In the bottom two panels, two important rates are scaled by the amounts shown on the horizontal axis.

For $^{12}\text{C}^+$ and $^{13}\text{C}^+$

\[
\frac{dn(^{12}\text{C}^+)}{dt} = n(\text{CO})[n(^{13}\text{C}^+)k_f + n(\text{He}^+)k_{\text{He-CO}}] - n(^{12}\text{C}^+)[n(^{13}\text{CO})k_r + n(\text{H}_2) \sum_j k_{j-C^+} X_j]
\]

\[
\frac{dn(^{13}\text{C}^+)}{dt} = n(\text{CO})[n(^{12}\text{C}^+)k_r + n(\text{He}^+)k_{\text{He-CO}}] - n(^{13}\text{C}^+)[n(^{12}\text{CO})k_f + n(\text{H}_2) \sum_j k_{j-C^+} X_j].
\]

In each panel of Figure 2 the relative abundance $X(^{12}\text{C}^+)$ is shown by a solid (black) line and $X(^{13}\text{C}^+) \times R_{^{12}/^{13}}$ (the red dashed line) has been scaled up by the inherent isotopic abundance so that the gap between the solid black and dashed red lines shows directly the extent to which $^{13}\text{C}$ is depleted in $\text{C}^+$ and in the gas outside CO. The effect is generally very large at 10 K, though still somewhat below $\exp(35/T_K)$. The lower right panel shows the effect of artificially increasing the strength of the fractionation reaction, illustrating that depletion of $^{13}\text{C}^+$
might be a factor two stronger if competing reactions were less important.

Although the important chemical effects should be incorporated in the default model, its $^{13}\text{C}$ depletion (a factor 15) is much stronger than is seen even in CCH (at most a factor 4) and substantial $^{13}\text{C}$ depletion persists at relatively high temperature (the upper left panel). Of course none of this is observed. Lowering the C$^+$/13C$^+$ ratio can be accomplished ad hoc by assuming an undepleted metal abundance, by putting all the spare oxygen in a species like O$_2$ or OH that reacts rapidly with C$^+$, or by increasing the rate at which C$^+$ recombines with H$_2$ (lower left). Perhaps the least ad hoc modification is the case of small X(CO) because CO will eventually deplete from the gas phase. This modification is basically the effect suggested by Watson (1977) and modeled by Liszt (1978).

**APPENDIX C**

**IS CARBON FRACTIONATION REVERSIBLE AFTER FORMATION?**

In the fractionation chemistry, the ambient $^{13}\text{C}$ is depleted by a factor somewhat smaller than exp(35 K/$T_K$) corresponding to the binding energy difference in CO. In principle, if another molecule’s chemistry was dominated by a fractionation reaction like that of C$^+$ and CO, with an energy defect comparable to 35 K and an abundance much less than that of C$^+$ (which itself is not large) so that the gas contains sufficient amounts of $^{13}\text{C}$, that molecule’s complement of $^{13}\text{C}$ could be restored to a degree approaching the abundance ratio inherent in the gas, $R_{12/13}$. At present, it is not possible to demonstrate that such in situ fractionation after formation occurs for any species beside CO: species either react chemically with C$^+$ to form other species or they react too frequently with other things beside C$^+$, with the added complication that the rate constants of the required fractionation reactions are still unknown even 35 years since the importance of the CO fractionation reaction was established. CS is in fact one of the better chemical candidates, with an energy difference between CS and $^{13}\text{CS}$ of 26.3 K, but the fractionation reaction with C$^+$ has never been measured.

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