

CARBON ISOTOPIC CHEMISTRY

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ABSTRACT. Isotopic molecular abundances are used to interpret Galactic chemical evolution and the properties of interstellar clouds. The isotopic chemistry of carbon plays an important role in the interpretation of these measurements. This paper reviews the recent measurements of the carbon twelve to thirteen ratio across the Galaxy and the isotopic chemistry.

1. Introduction

For twenty years isotopic abundances of molecules in interstellar clouds (ISC) have been measured by radio and optical techniques. These observations are important to: (1) determine Galactic chemical evolution (nucleosynthesis, star formation rate, injection and mixing of gas in the interstellar medium); (2) interpret physical conditions in ISCs; (3) test models of interstellar chemistry; and, (4) study the chemical evolution of the solar system. Carbon isotopic species are especially important because carbon molecules are pervasive and important probes of ISCs, the chemistry is reasonably well understood, and twelve and thirteen carbon trace primary and secondary nucleosynthesis, respectively. Here I review carbon isotopic ratio measurements and discuss the basic elements of the carbon isotopic chemistry

2. Observations of Carbon Isotopic Ratios

Across the Galaxy carbon isotopic ratios have been measured in the radio, mainly with CO and H₂CO, and locally (< 1 kpc) also measured in the optical with CH⁺ and CN. CO is pervasive and easily observed in emission, however the most abundant isotopes have large optical depths and good determinations of a ratio depend on detecting the very weak ¹³C¹⁸O and correcting for ¹²C¹⁸O opacity. Formaldehyde is observed in absorption towards strong continuum sources in its ¹²C and ¹³C isotopes. To use this species one must deal with the weakness of H₂¹³CO, photon trapping corrections for H₂¹²CO, and the uncertain effects of clumpiness on the trapping correction. In addition chemical processes can enhance isotopic ratios in these molecules. The optical absorption studies generally

have poor velocity resolution, though some high velocity resolution measurements have been made (limited to very bright nearby sources). The determination of ratios is complicated by baseline subtraction and line fitting (cf. Vladilo and Centurion 1991). Isotopic enhancement is probably not important for CH^+ formation towards these sources, but may be a factor for CN and CO .

To address the issue of the carbon isotopic ratio across the Galaxy, Langer and Penzias (1990; hereafter LP90) recently presented a study of nine interstellar clouds observed in the rare and doubly rare isotopes of carbon monoxide, $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{18}\text{O}$. The use of low abundance species minimizes radiative transfer effects, and observations towards dense shielded cores reduces complications from isotopic chemical and photodissociation enhancements. They found a systematic gradient in the $^{12}\text{C}/^{13}\text{C}$ ratio across the Galaxy from ≈ 30 in the inner part at 5 kpc to ≈ 70 at 12 kpc. This trend is similar to that derived from formaldehyde observations (Henkel, Wilson, and Beiging 1982), however the formaldehyde ratios are generally higher across the disk, and show more scatter than the CO measurements. Both the CO and formaldehyde indicate a Galactic Center value about 24. Figure 1 displays the isotope ratio from formaldehyde and carbon monoxide across the Galaxy as a function of distance, D , from the Galactic center) along with the corresponding linear fits ($^{12}\text{C}/^{13}\text{C}$ proportional to $5.6 D(\text{kpc})$ for H_2CO and $5.9 D(\text{kpc})$ for CO)

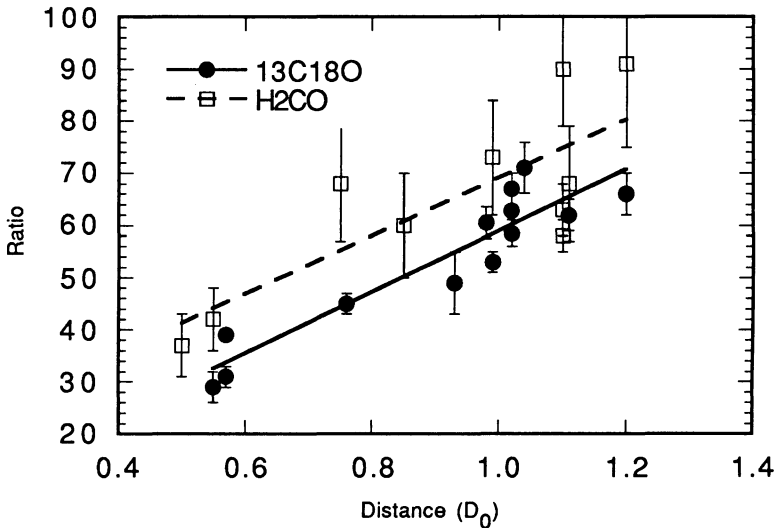


Fig. 1. Carbon 12 to 13 isotope ratio across the Galaxy using H_2CO (Henkel et al. 1982) and CO (LP90 and LP91) data, where distance is with respect to Solar distance D_0 .

In the local solar neighborhood LP90 derived an average value $^{12}\text{C}/^{13}\text{C} = 57 \pm 3$ from the Galactic gradient, although individual sources ranged from 49 to 67 (excluding 79 in the Orion A K-L region because the strong nearby HII region produces photodissociation enhancement effects). Because there are a wide variety of techniques and species available for measuring the ratio in the solar neighborhood accurate determinations in this region are

particularly important for fixing the local value, thereby establishing absolute values across the Galaxy.

To improve the value for the carbon isotope ratio in the local solar neighborhood Langer and Penzias (1991; hereafter LP91) extended their $^{13}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ study to three sources not known to be associated with HII regions or strong UV radiation fields: B5, B335, and L134N (also known as L183). In addition they observed another position in Orion far from the HII region near K-L. A sample spectrum from B5 is shown in Figure 2. In the four sources the ratio ranges from 58 to 71 with a weighted average of 61 ± 2 (plotted in Figure 1), slightly larger than the value of 57 suggested in the earlier work on the Galactic gradient. The local value of 61 ± 2 derived from CO is considerably smaller than the formaldehyde result of 80 ± 7 , as well as the terrestrial value of 89.

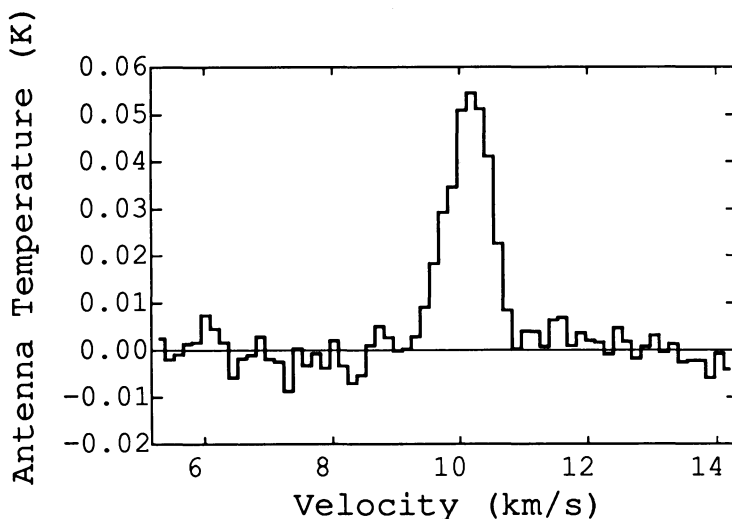


Fig. 2 Spectrum of $^{13}\text{C}^{18}\text{O}$ in the source B5.

The optical measurements of the isotope ratio have improved in recent years but also show considerable differences among various observations of CH^+ and CN . Kaiser, Hawkins, and Wright (1991) summarize recent optical observations in the local solar neighborhood (see their Table 1). The isotope value derived from CH^+ is not without controversy. Stahl et al. (1989), Crane et al. (1991), and Stahl and Wilson (1991) find a value about 67 ± 2 , in agreement with earlier (but less accurate) measurements. While the measurements of Hawkins et al. (1985) and Hawkins and Jura (1987) yield 42 ± 7 . CN absorption line observations of Crane and Hegyi (1988) yield 47 ± 5 . Furthermore, Hawkins and Jura (1987) derive a local value of 43 ± 4 from averaging several CH^+ sources within a kpc. Recently Vladilo and Centurion (1991) suggested that the data analysis approach of Hawkins and co-workers could overestimate the equivalent width for $^{13}\text{CH}^+$ by a factor of two, perhaps explaining the lower values. It also differs somewhat from the best values derived from the CH^+ absorption measurements of the nearby cloud Zeta Oph, 71 ± 3 (Stahl and Wilson 1991) to 67 ± 2 (Crane et al. 1991).

These radio and optical results raise the following important questions. 1) Why are there differences between the CO and H₂CO? (2) Why do CN and CH⁺ isotope ratios differ? The answer may lie in the details of the isotopic chemistry.

3. Carbon Isotopic Chemistry

Isotopic reactions are important both in shielded regions where cosmic ray ionization drives the ion molecule chemistry of carbon and in translucent or PDR regions where UV radiation is important. In dense shielded regions cosmic rays produce H₃⁺ ions which through their interactions with O and C initiate molecule production. Most of the carbon ends up as CO (assuming there is more gaseous oxygen available than carbon), with small amounts found in other molecules such as formaldehyde, CS, and CN. A wide variety of neutral-neutral, electron recombination, and ion-molecule reactions are involved in the chemistry once the initiating steps are taken (cf. Prasad and Huntress 1980; Langer et al. 1984; Langer and Graedel 1989). Helium ions destroy the stablest molecules and in the case of CO produce carbon ions. The balance between H₃⁺ converting carbon and oxygen atoms into molecules and He⁺ destroying the most stable molecules CO, O₂, and H₂O, for example, determines the relative abundance of atomic to molecular form. Isotopic exchange reactions can significantly alter the isotopic abundance of these molecules. For carbon the isotopic exchange reaction (Watson, Anicich, and Huntress 1976),



can enhance the ¹³CO abundance, particularly at low temperatures, but only if this reaction is an important pathway for producing CO. In dense shielded regions almost all available carbon is in CO and the CO isotope ratio reflects the elemental isotopic ratio, ¹²CO/¹³CO ≅ ¹²C_{true}/¹³C_{true}. This result does not necessarily hold true for the other carbon molecules. The destruction rate of ¹³C⁺ is larger than that for ¹²C⁺ and therefore less thirteen carbon (in the form of ions and neutrals) is available to form other molecules through the non-isotope exchange reactions (cf. detailed discussion in Langer et al. 1984). Therefore, H₂¹²CO/H₂¹³CO, H¹³CN/H¹³CN, etc. < ¹²C_{true}/¹³C_{true}. Model calculations (Langer and Graedel 1989) show that formaldehyde can be enhanced in the twelve carbon species by up to a factor of two even when CO is not (or only slightly) enhanced with respect to thirteen carbon species. This aspect of the isotopic chemistry may explain the difference in the isotopic ratios derived from CO and formaldehyde in the Galactic surveys, but more observations are needed to confirm this explanation.

In UV dominated regions (cloud edges, PDRs) there is sufficient UV to keep some carbon ionized and therefore the isotopic exchange reaction can be very important for CO. In addition, CO is photodissociated by line absorption and self-shielded to different degrees depending on their relative abundances (cf. Bally and Langer 1981; van Dishoeck and Black 1988). Under such conditions the less abundant species may be isotopically underabundant relative to the more abundant species and the observed isotope ratios will not reflect the true elemental isotopic ratio. This regime of the interstellar chemistry has been extensively modeled by van Dishoeck and Black (1988). Their models confirm that combinations of isotopic exchange and self-shielding lead to varying degrees of enhancement in both ¹²CO and ¹³CO.

In the UV regions this variability of CO enhancement can also impact the isotopic abundances of the other carbon molecules. Any isotopic enhancement of CO (no matter

which isotope) results in the reverse enhancement in the exchange ion C^+ and hence its direct products, such as CH and CH_2 . In addition, for CN there is the possible exchange reaction,



which will be important when it competes with photodestruction of CN. A simple model of CN formation from reactions of N with CH, CH_2 , C_2 , and C_2H (whose sum is denoted by CM) leads to the following relationship for the carbon isotopic ratio of CN,

$$[^{12}CN/^{13}CN] \approx [^{12}CM/^{13}CM] \frac{[\Gamma(CN) + k_f n(^{12}C^+) + k_0 n(O)]}{[\Gamma(CN) + k_r n(^{12}C^+) + k_0 n(O)]}$$

where, Γ , is the photodestruction rate, k_f and k_r are the forward and reverse isotope exchange reaction rate coefficients, k_0 the neutral-neutral reaction rate coefficient with oxygen, and $n(X)$ the density of species X. From this expression it can be seen that the CN isotope ratio can be enhanced either in twelve or thirteen C depending on conditions. The isotope exchange chemistry for CN may explain the variability in the CN observations and the differences between the CN and CH^+ isotope ratio in the same sources. CH^+ is not expected to be isotopically enhanced since it is thought to be formed under high temperature conditions where the difference in isotopic rates is unimportant.

4. References

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