We present high signal-to-noise ratio observations of optical transitions in CN and CH\textsuperscript{+} for a number of Galactic diffuse clouds. The data are examined to extract the \(^{12}\)CN/\(^{13}\)CN and \(^{12}\)CH\textsuperscript{+}/\(^{13}\)CH\textsuperscript{+} ratios along each line of sight in order to assess predictions of diffuse cloud chemistry. We find a weighted mean \(^{12}\)CH\textsuperscript{+}/\(^{13}\)CH\textsuperscript{+} ratio of 74.4 ± 7.6. This result is consistent with the average \(^{12}\)C/\(^{13}\)C ratio of 70 ± 7 for local interstellar clouds, confirming the theoretical expectation that \(^{12}\)CH\textsuperscript{+}/\(^{13}\)CH\textsuperscript{+} represents the ambient carbon isotopic ratio. Our sample includes three sight lines for which previous studies had found much lower values of \(^{12}\)CH\textsuperscript{+}/\(^{13}\)CH\textsuperscript{+} that are not confirmed here. Thus, we find no evidence for variation in \(^{12}\)C/\(^{13}\)C within 1 kpc of the Sun. The 12-to-13 ratios in both CN and CO, however, show significant fractionation away from the ambient value due to the opposing effects of photodissociation and charge exchange reactions. Our \(^{12}\)CN/\(^{13}\)CN measurements are combined with determinations of \(^{12}\)CO/\(^{13}\)CO from the literature to enable a detailed analysis of the effects of chemical fractionation in diffuse molecular clouds. We find suggestive evidence for an inverse relationship between \(^{12}\)CN/\(^{13}\)CN and \(^{12}\)CO/\(^{13}\)CO, resulting from the physical association of CN and CO in the cores of the clouds. Additionally, the isotopolog ratio examined here suggest that about 20 percent of C is locked up in CO in typical diffuse cloud cores, while up to 85 percent may reside in CO in the central portions of the Ophiuchus diffuse clouds. Finally, we examine rotational excitation temperatures in both \(^{12}\)CN and \(^{13}\)CN. Our weighted mean value of \(T_{\text{rot}}\) (\(^{13}\)CN) = 2.754 ± 0.002 K implies an excess over the cosmic microwave background (CMB) of only 29 ± 3 mK, considerably smaller than some recent surveys have suggested. This modest excess can be accounted for if collisional excitation by electrons is occurring locally in some clouds, with derived electron densities of \(n_e = 0.1 - 0.5 \, \text{cm}^{-3}\). Yet, given the dispersion of 134 mK in our individual \(T_{\text{rot}}\) measurements, the excess may not be physical. There is some indication of a greater excess in \(T_{\text{rot}}\) (\(^{13}\)CN) based on our weighted mean of 2.847 ± 0.014 K, but the dispersion in these measurements is also greater (259 mK). The rotational excitation temperature observed in \(^{13}\)CN, via the \(R(0), R(1),\) and \(P(1)\) lines, shows no excess over the CMB.