**OBSERVATIONS OF C\textsubscript{3} IN TRANSLUCENT SIGHT LINES**

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**ABSTRACT**

The $^1\Pi_u^+ \leftarrow X^1\Sigma^+_g$ transition of the simplest polyatomic carbon chain molecule, C\textsubscript{3}, at 4051.6 Å has been searched for toward reddened stars where abundant C\textsubscript{2} had been reported and toward other stars with high color excess. Absorption from C\textsubscript{3} has been detected toward 15 stars with color excesses $E(B-V)$ from 0.33 to 1.12. The observed C\textsubscript{3} column densities, ranging from $10^{12}$ to $10^{13}$ cm\textsuperscript{-2}, are well correlated with the corresponding C\textsubscript{2} column densities, with $N(C_2)/N(C_3) \sim 40$, indicating their close chemical relation. The carbon-rich sight line toward HD 204827 (for which no previous C\textsubscript{2} observation had been reported) has by far the highest C\textsubscript{3} and C\textsubscript{2} column densities. The chemistry of formation of C\textsubscript{3} from C\textsubscript{2} is discussed. A search for the next strongest 020–000 vibronic band was unsuccessful as a result of the low Franck-Condon factor and interference with a stellar line. Searches for C\textsubscript{4} and C\textsubscript{5} were negative.

**Subject headings:** astrochemistry — ISM: lines and bands — ISM: molecules

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1. **INTRODUCTION**

The recent detection by Maier et al. (2001) of the absorption at 4051.6 Å of C\textsubscript{3} in diffuse interstellar clouds, toward the reddened stars ζ Ophiuchi, 20 Aquilae, and ζ Persei, has demonstrated the abundance of this simplest polyatomic carbon chain molecule, which had been sought in the diffuse interstellar medium for many years (Clegg & Lambert 1982; Snow, Seab, & Joseph 1988; Haffner & Meyer 1995). The obtained C\textsubscript{3} column densities of $(1-2) \times 10^{12}$ cm\textsuperscript{-2} are higher than the predicted values in the comprehensive model calculations by van Dishoeck & Black (1986) by several orders of magnitude and are closer to that predicted by the simpler calculation of Clegg & Lambert (1982). Subsequently, C\textsubscript{3} has been observed toward the more reddened star HD 210121 with a C\textsubscript{3} column density of $3.8 \times 10^{12}$ cm\textsuperscript{-2} by Roueff et al. (2002). For many years, optical observations in the diffuse interstellar medium had been limited to atoms and diatomics. However, the recent observations of C\textsubscript{3}, along with the infrared observations of H\textsubscript{2} (McCall et al. 1998, 2002; Geballe et al. 1999), mark the arrival of polyatomic molecular spectroscopy. Searches for longer carbon chain molecules C\textsubscript{4} and C\textsubscript{5} at 3788.6 and 5109.4 Å, respectively, by Maier, Walker, & Bohlender (2002) in ζ Ophiuchi were negative.

The 34051.6 band of C\textsubscript{3} was first noted in emission in William Huggins’ plate of comet Tebbutt (Huggins 1881, 1882) and has since been observed in many comets (for early works see Bobrovnikoff 1931, 1942). The spectrum was also observed in absorption in photospheres of the N-type carbon star YCVn (McKellar 1948) and other cool stars (for a review see Jørgensen 1994). The carrier of the spectrum was identified to be C\textsubscript{3} in a laboratory experiment by Douglas (1951), and the transition was assigned to $^1\Pi_u^+ \leftarrow ^1\Sigma^+_g$ by Gausset et al. (1963). The absorption has been seen strongly in CRL 2688 (Crampton, Cowley, & Humphreys 1975), as well as in other carbon-rich protoplanetary nebulae (Hrivnak & Kwok 1999). C\textsubscript{3} has also been observed through its infrared spectrum at 4.9 μm, corresponding to the antisymmetric C–C stretching vibration, in the circumstellar material around the late-type carbon star IRC +10216 (Hinkle, Keady, & Bernath 1988), and through its far-infrared absorption spectrum at 157 μm, corresponding to the anomalously low bending vibration, toward Sagittarius B2 and IRC +10216 (Cernicharo, Goicoechea, & Caux 2000) with the high column densities of $6 \times 10^{15}$ and $2 \times 10^{16}$ cm\textsuperscript{-2}, respectively. Recently Giesen et al. (2001) published one line [R(2)] of the far-infrared spectrum observed in high spectral resolution with the Kuiper Airborne Observatory that had initially been reported in 1995.

We report here our observations of the C\textsubscript{3} absorption spectrum in the diffuse interstellar medium in translucent sight lines (often defined to have visual extinctions between 1 and 5 mag). The resolving power ($R = 37, 500$) of our Astrophysical Research Consortium Echelle Spectrometer (ARCES) is not sufficient to resolve individual rotational lines as was successfully accomplished with the Gecko echelle spectrograph used by Maier et al. (2001; with $R = 121, 000$) and by the UV–Visual Echelle Spectrograph used by Roueff et al. (2002; $R = 69, 000$), but it allows us to obtain spectra of stars that are fainter in the violet. We have detected the C\textsubscript{3} spectrum toward stars with high color excesses, such as HD 169454 [$E(B-V) = 1.12$] and HD 204827 [$E(B-V) = 1.11$], in contrast to the stars with $E(B-V) = 0.31$–0.33 studied by Maier et al. (2001) and $E(B-V) = 0.40$ by Roueff et al. (2002). The observed C\textsubscript{3} column densities are higher. Although our low instrumental resolution makes the sensitivity of detection considerably lower and does not allow us to determine the temperature of individual clouds accurately, the C\textsubscript{3} column densities can be measured with a reasonable accuracy by comparing observed spectra with simulated spectra.

2. **OBSERVATIONS**

Observations were carried out using the ARCES spectrometer attached to the 3.5 m telescope at the Apache Point

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Observatory (APO). Data reduction was done by using standard IRAF routines as described in detail by Thorburn (2000) and Wang et al. (2002). Because of the observed (Maier et al. 2001) and expected good correlation between column densities of C2 and C3, the program stars were chosen from a star sample toward which high column densities of C2 had been reported. Since its discovery toward Cygnus OB2 No. 12 (Souza & Lutz 1977), C2 has been observed toward over 50 stars. The C2 column densities, originally reported in many papers, are tabulated in four papers, that is, van Dishoeck & Black (1989), Crawford (1990), Federman et al. (1994), and Gredel (1999).

We have also examined other reddened sight lines with \( E(B-V) > 0.4 \) for which observations of C2 had not previously been reported but which might be expected to have high C2 column densities. In connection with our extensive, ongoing survey of the diffuse interstellar bands, we have obtained spectra of almost all the stars accessible from APO toward which C2 has been detected and also of many other stars with color excesses between 0.4 and 1.12 mag. Our survey has aimed at achieving a signal-to-noise ratio (S/N) of 1000 near 5800 Å, but we further integrated on selected stars to have high S/N in the violet. Two sight lines for which C2 had not previously been reported have shown the C3 absorption lines. Strong C2 absorption has been observed toward both sight lines. In fact, HD 204827 (which showed by far the highest C3 column density) belonged to this group of stars. A particularly long integration (9.5 hr) has been used for this sight line.

The observed stars, their spectral types, visual magnitudes, color excesses, distances, and dates of observation are summarized in Table 1. This table is limited to stars toward which C3 has been detected and those toward which C2 has been detected for the first time. A total of 39 other sight lines have also been examined as discussed later in § 4.1.

### 3. SPECTRAL SIMULATION

Since individual rotational lines are not resolved in our observations, we determined C3 column densities by comparing simulated and observed spectra. For this purpose we used the wavelengths reported by Gausset et al. (1965) and the Höl-London intensity factors for a perpendicular band (\( \Lambda = 1 \rightarrow 0 \), i.e., \( (J+2)/2(J+1) \), \( \frac{1}{2} \), and \( (J-1)/2(J+1) \) for the R-, Q-, and P-branch lines, respectively.

The distribution of molecular population in individual rotational levels is a complicated problem for nonpolar molecules like C2 and C3 since a subtle balance of the radiative and collisional pumping rates and the formation and destruction rates of the molecules needs to be considered (van Dishoeck & Black 1982). Maier et al. (2001) have reported a two-temperature distribution for C3 in ζ Oph corresponding to a low temperature \( T_l = 60 \) K for lower rotational levels (\( J = 0-12 \)) and a high temperature \( T_h = 230 \) K for higher levels with \( J \geq 12 \). Such a distribution has also been reported for C2 toward other stars (Lutz & Crutcher 1983). Roueff et al. (2002) applied a much more

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**TABLE 1**

<table>
<thead>
<tr>
<th>Star</th>
<th>Name</th>
<th>Type</th>
<th>( V )</th>
<th>( E(B-V) )</th>
<th>( D ) (pc)</th>
<th>Date (UT)</th>
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<td>B3 V</td>
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<td>B2.5 Ibe</td>
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<td>B5 V</td>
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<td>...</td>
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<td>...</td>
</tr>
</tbody>
</table>

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* The distances to stars have been estimated by one of us (L. M. H.). For nine of the 24 stars listed for which \( \text{Hipparcos} \) parallaxes of 4 \( \sigma \) precision or better are available, the distances were derived from these parallaxes. For the other 15 stars, the distances were estimated from the photometry, the spectral types, and an adopted value \( Av \).

b The date of observation is given in the order of month-day-year.

\( \text{UT} \): Universal Time

\( \text{V} \): Visual magnitude

\( E(B-V) \): Color excess

\( D \): Distance (parallax)

\( \text{Date (UT)} \): Date of observation in UT

\( \text{Star Name} \): Name of the star

\( \text{Type} \): Spectral type

\( \text{V} \): Visual magnitude

\( E(B-V) \): Color excess

\( D \): Distance (parallax)

\( \text{Date (UT)} \): Date of observation in UT

\( \text{Star Name} \): Name of the star

\( \text{Type} \): Spectral type

\( \text{V} \): Visual magnitude

\( E(B-V) \): Color excess

\( D \): Distance (parallax)

\( \text{Date (UT)} \): Date of observation in UT

Available at http://www.apo.nmsu.edu/instruments/echelle.
sophisticated analysis to their observations of C3 toward HD 210121. In view of the difficulty and uncertainty of such analysis, the lack of rotational resolution in our spectra, and the relatively lower temperature of our sources (see below), we here use the simplest assumption of a one-temperature rotational distribution.

Examples of simulated spectra are compared with the observed spectrum toward HD 204827 in Figure 1. Figure 1a shows a simulated spectrum using the resolution of 110,000 used by Maier et al. (2001) at T = 40 K. Figure 1b gives the same spectrum simulated for our observational conditions, i.e., resolution of 34,000 and S/N of 900. Figure 1c shows the observed spectrum of HD 204827. Figure 1d shows a simulated spectrum at the same conditions for Figure 1b, except that the two-temperature distribution of Maier et al. (2001) is used. The temperature of T = 40 K is used in Figures 1a and 1b because of the observed sharpness of the central Q-branch pileup. Simulations at T1 = 60 K of Maier et al. (2001) and T1 = 65 K of Roueff et al. (2002) yield a considerably broader Q-branch feature. In addition, our C2 spectrum toward this star shows rotational fine structure with the excitation temperature of ~40 K. If we use the two-temperature population distribution of Maier et al. (2001), i.e., T1 = 60 K and T2 = 230 K (Fig. 1d), or that of Roueff et al. (2002), the simulated spectrum shows a visible R-branch head at 4049.6 Å whose intensity is a sizable fraction of the Q-branch pileup (Fig. 1d).

Examples of the observed C3 spectra are shown in Figure 2. The line of sight toward HD 204827 shows by far the strongest absorption. While no C2 observation had previously been reported, our APO spectrum has revealed a very high C2 column density of (4.4 ± 0.3) × 1014 cm−2 toward this star with E(B−V) = 1.11. This C2 column density is comparable to that toward the much more heavily reddened star Cygnus OB2 No. 12 with E(B−V) = 3.31, reported to be 3.8 × 1014 cm−2 by Lutz & Crutcher (1983) and 3.4 × 1014 cm−2 by Grebel, Black, & Yan (2001). All quoted C2 column densities are based on an oscillator strength of 1.0 × 10−3 for the 2−0 band; van Dishoeck & Black 1989.) Evidently the interstellar gas toward HD 204827 is extraordinarily rich in carbon molecules.

In total, we have detected C3 absorption toward 15 stars. The observed equivalent widths, Wλ, are listed in Table 2 together with the time of integration and the observed S/N in the continuum near 4051.6 Å. The uncertainties in the table correspond to 1 σ, while the lower limit corresponds to 3 σ. The Wλ values toward three stars with “≤” signs represent tentative detections. Note that our Wλ values represent half of the total equivalent width of the band, since we measured only the pileup of the Q-branch lines (which accounts for approximately half of the total absorption). We have assembled in this table stars toward which C3 has been detected, including those by Maier et al. (2002), and stars toward which C2 has been detected for the first time. We have detected C3 toward HD 179406 (20 Aql) reported by Maier et al. (2001), but we have not been able to detect C3 toward the other two stars (ζ Oph and ζ Per) where very clear spectra of C3 were reported by Maier et al. (2001). This indicates the lack of sensitivity of our observations (because

4. RESULTS AND ANALYSIS

4.1. Observed Spectra

4.1. Observed Spectra

Fig. 1.—(a), (b), and (d) Simulated spectra of the λ4051.6 band of C3 compared with (c) the observed spectrum toward HD 204827. (a) is for the high resolution of R = 110,000 and no noise, while (b) and (d) are for R = 34,000 and S/N = 900 simulating our observed conditions at the APO. A temperature of T = 40 K is used for (b), while a two-temperature distribution of T1 = 60 K and T2 = 230 K is used for (d) (see text).
of our lower resolution) and also illustrates the higher column densities of C$_3$ toward the stars where we have detected it.

There are three sight lines in which large C$_2$ column densities have been reported, and yet detections of C$_3$ are not as straightforward as in other sight lines. For HD 29647 with $N$(C$_2$) = 1.7 × 10$^{14}$ cm$^{-2}$ (Hobbs, Black, & van Dishoeck 1983) and HD 26571 with $N$(C$_2$) = 1.1 × 10$^{14}$ cm$^{-2}$ (Federman et al. 1994), narrow, blended stellar features made the detection of the weak C$_3$ absorption difficult and the measured column density less reliable. For HD 147889 with $N$(C$_2$) = 1.2 × 10$^{14}$ cm$^{-2}$ (Crutcher & Chu 1985), we set an upper limit of $W_\lambda < 3.0$ mA corresponding to the C$_3$ column density (2.6 × 10$^{12}$ cm$^{-2}$), which is lower than the upper limit reported by Haffner & Meyer (1995; 4 × 10$^{12}$ cm$^{-2}$).

There are 39 sight lines other than those listed in Table 2 in which the C$_3$ absorption was not detected. They are given in footnote a of the table with the upper limit of the equivalent width in mA in parentheses.

The strong C$_3$ and C$_2$ absorption toward HD 204827 prompted us to look for the 020–000 vibronic band, which is 7–9 times weaker than the 000–000 origin band as discussed in § 3. Unfortunately, the band partially overlaps with a strong stellar atomic line in HD 204827 and was not clearly detected. This band should be detectable toward stars with less atomic absorption, using higher spectroscopic resolution.

We have also looked for the spectral lines of C$_4$ and C$_5$ at 3788.6 and 5109.4 Å, respectively, which were looked for toward ζ Ophiuchi by Maier et al. (2002). The spectra have not been detected, setting the upper limit for the equivalent width of 2.6 and 1.2 mA (3 $\sigma$), respectively, toward HD 204728. If we use the same oscillator strengths as assumed by Maier et al. (2002), they correspond to upper limits for the C$_4$ and C$_5$ column densities of 2 × 10$^{14}$ and 5 × 10$^{12}$ cm$^{-2}$ (3 $\sigma$), respectively. Maier et al. (2002) note that the λ5109 band system of C$_3$ is a forbidden transition and that there is a stronger band system corresponding to the $^1\Pi_u - ^1\Sigma^+_g$ transition that has been measured in their 5 K neon matrix at 4454 Å and is 5 times more intense than the λ5109 band. Since the gaseous wavelength of this transition is not known, we have examined spectra of HD 204827, HD 169454, HD 172028, and HD 206267, which showed strong C$_3$ spectra, to see if there is a matching absorption in the wavelength region from 4432 to 4476 Å (corresponding to a matrix shift of ±0.5%), without success. A gas-phase laboratory observation of this transition is eagerly waited. Although HD 204827 ($V = 7.94$) is much fainter than ζ Ophiuchi ($V = 2.56$), an order of magnitude higher observed column densities of C$_2$ and C$_3$ in HD 204827 make it a better candidate to look for C$_4$ and C$_5$ at low resolution and high sensitivity since in any case the rotational structure of the heavier carbon chains is not resolved.

4.2. Column Density

The C$_3$ column densities were obtained using the formula

$$N = \frac{2m_e e_2 W_\lambda}{\pi e_2 \lambda f} = (2.26 \times 10^{12} \text{ cm}^{-1}) \frac{W_\lambda}{\lambda f}$$

(Spitzer 1978). The extra factor of 2 in front of $W_\lambda$ is the result of observing only the $Q$-branch pileup. We assume that the loss of intensity from the pileup due to $Q$-branch lines with high $J$-values that appear outside of the central feature is approximately compensated by the $P(2)$ and $P(4)$ lines that are blended in the pileup.

The value of the oscillator strength $f$ has been controversial. Theoretical values of the oscillator strength of the electronic transition $f_{1u}$ are converging to 0.50 (Chabalowski, Bueker, & Peyerimhoff 1986), but they are much higher than the experimental value of 0.0246 (Becker, Tatarczyk, & Peric-Radic 1979), which claims high accuracy. The Franck-Condon factor of the 000–000 band has been calculated to be 0.741 (Peric-Radic et al. 1977) or 0.615 (Jungen & Merer 1980). Here we use $f = 0.016$, which is approximately equal to the product of the experimental $f_{1u}$ and the theoretical Franck-Condon factor, just to be consistent with Maier et al. (2001). Roueff et al. (2002) used $f = 0.0146$. Future variations of the oscillator strength will change the estimate of the column densities accordingly.

The calculated C$_3$ column densities are listed in Table 2. In order to explore the correlations between C$_3$ and other species, the observed column densities of C$_2$, CH, and CN are also listed in the table. For the C$_2$ column densities, previously reported values normalized to the oscillator strength of 1.0 × 10$^{-3}$, as well as our measured values from APO, are listed. In general they are in agreement, but some differ significantly. The CH and CN column densities have been compiled from various references in the literature or have been derived from our ARCES spectra as noted in footnote a of the table.
The C₃ column densities and the color excess shown in Figure 2 are directly proportional to each other, but the correlation coefficient is not as good, with correlation coefficients of 0.576 and 0.626, respectively.

The C₃ column densities and the color excess shown in the bottom right-hand panel of Figure 3 have a correlation coefficient of 0.728. In this figure we use only sight lines where C₃ has been detected; if we take into account other sight lines, the correlation coefficient is considerably lower. There are carbon-poor sight lines with high \( E(B-V) \) and strong diffuse interstellar absorption bands (DIBs) but with no detectable C₂ and C₃, such as toward HD 193143 (\( E(B-V)=1.27 \)) and HD 20041 (\( E(B-V)=0.72 \)). It is interesting to note that high column densities of \( H₂ \), \( 2.3 \times 10^{14} \) cm⁻² and \( 3.5 \times 10^{14} \) cm⁻², respectively, have been observed along those lines of sight (McCall et al. 2002). This indicates that the chemistry of C₂ and C₃ is completely decoupled from the chemistry of \( H₂ \). Our extensive data set of the DIBs has...
led to the observation that there is a family of DIBs that is enhanced in the lines of sight with high C2 and C3 column densities. These findings are discussed in a separate paper (Thorburn et al. 2003).

5. CHEMISTRY OF C3

The observed strong correlation between \(N(C_3)\) and \(N(C_2)\) suggests that C3 and C2 are in the same chain of chemical reactions. Based on previous studies of the chemistry of C3 (Mitchell, Ginsburg, & Kuntz 1978; Clegg & Lambert 1982), the following chains of reactions are considered (see Fig. 4).

These chains of reactions include four types of chemical reactions involving the three abundant chemically active species in the diffuse interstellar medium (H2, C+, and electrons) as well as photons. To obtain an order-of-magnitude estimate of the various reaction rates, we assume typical number densities of \(n(H_2) = 10^2\) cm\(^{-3}\) and \(n(C^+) = n(e) = 10^{-2}\) cm\(^{-3}\). We also adopt the general Langevin rate constant of \(10^{-9}\) cm\(^3\) s\(^{-1}\) for ion-neutral reactions and an electron recombination rate constant of \(10^{-7}\) cm\(^3\) s\(^{-1}\). The hydrogen abstraction reaction

\[
X^+ + H_2 \rightarrow XH^+ + H
\]

is the fastest with a rate of \(\sim 10^{-7}\) s\(^{-1}\) except for \(X^+ = C_2H_2^+, C_2H_3^+,\) and \(C_3H^+\), which will be discussed below. The electron recombination reaction

\[
XH^+ + e \rightarrow X + H
\]

is next with a rate of \(\sim 10^{-9}\) s\(^{-1}\), and the chain building reaction

\[
XH + C^+ \rightarrow XC^+ + H
\]

is the slowest, with a rate of \(\sim 10^{-11}\) s\(^{-1}\). The photoionization rate of C2 seems to be poorly determined, but an estimate of \(10^{-10} \exp(-2A_\nu)\) s\(^{-1}\) has been used (Mitchell et al. 1978).

Hydrogen abstraction reactions of three carbocations have especially low rates, and their competition with the electron recombination rate has to be considered separately. The reaction of C2H2\(^+\) is highly endothermic (\(\sim 2.7\) eV), and its rate is negligible. The rate constant of the reaction

\[
C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H
\]

has been controversial. If we use the rate reported by Smith & Adams (1977), which is lower than the Langevin rate by 2 orders of magnitude, the reaction is competitive with the dissociative recombination of C2H2\(^+\) and hence the branching of the chain in Figure 4. Ab initio theory even predicts that the reaction is slightly \((0.08 \pm 0.08\) eV) endothermic (Maluendes, McLean, & Herbst 1994) although there is a conflicting experimental report (Hawley & Smith 1992).
Future astronomical observations of either C$_2$H or C$_2$H$_2$ in the chain may settle this controversy. The reaction

$$C_3H^+ + H_2 \rightarrow C_3H_2^+ + H$$

has been shown to be slightly endothermic and slower than the radiative association reaction

$$C_3H^+ + H_2 \rightarrow C_3H_2^+ + h\nu$$

by Maluendes, McLean, & Herbst (1993). The rate of this reaction, $9 \times 10^{-12}$ cm$^3$ s$^{-1}$ (E. Herbst 2002, private communication), is slower than the electronic recombination, but this reaction may be an important channel to cyclic C$_3$H$_2$ (Maluendes et al. 1993).

In the chemical flow chart of Figure 4, molecules with a low destruction rate (i.e., by chain building with C$^+$ and photoionization) are abundant. Simple steady state chemical kinetics indicate that the neutral molecules C$_2$, C$_2$H, C$_2$H$_2$, and C$_3$ (the main destruction mechanism of C$_3$ is photoionization/dissociation) are more abundant than the ionic species by at least 2 orders of magnitude. It will be interesting to observe C$_2$H in the radio and/or C$_2$H$_2$ in the ultraviolet in the same sight lines where C$_2$ and C$_3$ have been observed.

The flow of chain reactions is reduced at each juncture by other reactions that branch out from it. They include photodissociation and ionization, electron recombination, reactions with oxygen atoms, and other ion-neutral reactions. The small value of $N(C_3)/N(C_2) \approx 1/40$ is due to those reductions and the photodissociation of C$_3$ back to C$_2$.

6. SUMMARY

We have detected the C$_3$ 4051.6 spectrum in 15 translucent sight lines. The observed C$_3$ column densities range from $1.0 \times 10^{13}$ to $1.2 \times 10^{12}$ cm$^{-2}$. As expected, the observed C$_3$ column densities are well correlated with the C$_2$ column densities with $\langle N(C_2)/N(C_3) \rangle$ falling in $42 \pm 8$ for strong signals except one. The observation has revealed HD 204827 to be by far the most carbon-rich sight line, which makes it a good candidate to search for higher carbon chain molecules. For HD 206267, HD 207198, and HD 210121, for which column densities of both H$_2$ and H have been measured, the fractional abundances of C$_3$ are $x(C_3) \times 10^{10} = 7.9, 4.4$, and 11, respectively. It is interesting to study observationally and theoretically how carbon chains grow from C$_1$. Elongation of carbon chains using direct C$^+$ association followed by hydrogen abstraction reactions and recombination is slow for simple carbon molecules, but it becomes increasingly fast after C$_4$ (Freed, Oka, & Suzuki 1982).

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REFERENCES

——. 1942, Rev. Mod. Phys., 14, 164
Spitzer, L., Jr. 1978, Physical Processes in the Interstellar Medium (New York: Wiley)
Thorburn, J. 2000, UC Data Reduction Guide II