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# THE CARBON CHEMISTRY IN INTERSTELLAR CLOUDS TOWARD MODERATELY REDDENED STARS

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## ABSTRACT

Data on absorption from lines of CH, CN, $C_2$, and CO toward X Persei and stars in the Cepheus OB2 association have been obtained. These data have been combined with previously published data for the purpose of understanding the gas phase chemistry in moderately reddened directions. The conclusions presented by Federman and colleagues in 1984 for CN chemistry based on analytical expressions are strengthened through the analysis of a larger data set. A decrease in the abundance of $C^+$ is required to match the observational data for directions with $N(\mathrm{CH})$ approaching $10^{14}$ $\mathrm{cm}^{-2}$; carbon is predominantly in neutral gas phase species for such directions. When $N(\mathrm{CN})$ and $N(C_2)$ are compared with $N(\mathrm{CH})$ in a graphical manner, a possible change in slope occurs at $N(\mathrm{CH}) \approx 4\text{–}5 \times 10^{13}$ $\mathrm{cm}^{-2}$. A change in slope could signify a transition from a photochemical regime for directions with smaller column densities of CH to a chemical regime for directions with more CH. The CO results do not show any change in slope from a value of 2 over the entire range of column densities [$10^{13}$ $\mathrm{cm}^{-2} < N(\mathrm{CO}) < 10^{16}$ $\mathrm{cm}^{-2}$], indicating that the effects of CO self-shielding are more subtle.

*Subject headings:* interstellar: abundances — interstellar: matter — interstellar: molecules

## I. INTRODUCTION

The utilization of silicon photodiode detectors in recent years has made possible accurate determinations of the abundance of molecular species in diffuse interstellar clouds. Examples include the observations of CH (Federman 1982; Danks, Federman, and Lambert 1984), of $C_2$ (Chaffee *et al.* 1980; Hobbs 1981; Hobbs and Campbell 1982; Danks and Lambert 1983; van Dishoeck and de Zeeuw 1984), and of CN (Federman, Danks, and Lambert 1984). Models of the chemistry involving carbon for specific well-studied lines of sight (e.g., van Dishoeck and Black 1986) and for the average conditions in many lines of sight (Danks, Federman, and Lambert 1984; Federman, Danks, and Lambert 1984) have incorporated the results of the measurements. Although the theoretical models reproduce the data quite well, the above analyses have relied on observations toward stars with $E(B-V) \leq 0.4$ mag, where photochemistry dominates.

The most recent observational studies have concentrated on lines of sight toward nearby stars, which usually sample one predominant cloud, with $E(B-V)$ as large as 1.1 mag (Hobbs, Black, and van Dishoeck 1983; Lutz and Crutcher 1983; van Dishoeck and de Zeeuw 1984; Crutcher 1985; Crutcher and Chu 1985; Cardelli and Wallerstein 1986). These moderately reddened lines of sight are of interest chemically because the amount of extinction in the ultraviolet, which is the portion of the spectrum contributing to the photodissociation, is quite large, thereby lessening the role of photodissociation relative to chemical reactions in the destruction of molecules. The large amount of reddening for the nearby clouds also leads to the suggestion that gas densities are about $10^3$ $\mathrm{cm}^{-3}$, compared to a few hundred $\mathrm{cm}^{-3}$ for the previously studied directions; larger densities increase the importance of chemical reactions further. In the present work we analyze newly acquired and existing data in an attempt to ascertain the transition from the photochemical regime to the chemical regime.

The approach taken is similar to that taken in our previous studies (cf. Danks, Federman, and Lambert 1984; Federman, Danks, and Lambert 1984). An ensemble of directions is analyzed to derive general conclusions about the molecular chemistry. A slight modification to the approach is incorporated here: The column densities of CN, $C_2$, and CO are compared with the column density of CH. This modification is necessary because for most moderately reddened lines of sight, no direct measure of $N(H_2)$, the column density of $H_2$, is available. Since ion-molecule reactions involving $H_2$ lead to the formation of molecules containing carbon, nitrogen, and oxygen, correspondences between $N(H_2)$ and the molecules $N(\mathrm{CN})$, $N(C_2)$, and $N(\mathrm{CO})$ are expected. Cardelli and Wallerstein (1986) estimated $N(H_2)$ from $E(B-V)$ and found that the linear relationship between $N(\mathrm{CH})$ and $N(H_2)$ first deduced by Federman (1982) and Danks, Federman, and Lambert (1984) persists for directions with $N(H_2) \geq 2 \times 10^{21}$ $\mathrm{cm}^{-2}$. Moreover, Mattila (1986) showed from radio observations of CH in dark clouds that the relationship continues up to an $A_V$ of 4 mag [corresponding to $E(B-V) \approx 1.3$ mag and $N(H_2) \approx 4 \times 10^{21}$ $\mathrm{cm}^{-2}$].

The remainder of the paper is organized as follows. The data for CO toward HD 207198, for $C_2$ toward stars in the Cepheus OB2 association, including HD 207198, and for CH, CN, and $C_2$ toward X Persei are discussed in § II. The stars in Cepheus were studied because results already existed for CH and CN (Chaffee and Dunham 1979) and for CO (Tarafdar and Krishna Swamy 1982) toward two of the stars. Factors of 2 discrepancies in the measured equivalent widths of molecular absorption lines toward X Per (Frisch 1972; Cohen 1973; Lien 1984*a*) necessitated additional measurements before analyzing

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the data in terms of chemical models. Section III includes a presentation of the analysis of the available data for moderately reddened directions in terms of a chemical model based on gas phase reactions. The final remarks in § IV conclude the paper.

## II. DATA

### *a*) *Observations*

The ground-based observations were made with the coudé spectrometer of the 2.1 m telescope at McDonald Observatory in 1985 November and 1986 January. The data for the *B–X* lines of CH and CN near 3880 Å were obtained during the latter observing session; absorption from lines of the (2, 0) Phillips system of $C_2$ around 8775 Å was sought during both sessions. The resolving power of the spectrometer was set at 73,000 for the session in 1985 and was set at 30,000 for the 1986 observations. A Reticon detector with 1728 diodes was used. Examples of the spectra, both ultraviolet and optical, are shown in Figure 1; the slopes seen in the continua are from the background source.

The data for the *A–X* transitions of CO toward HD 207198 were taken from observations acquired with the *IUE* satellite. The archival data for the image SWP 17472 were obtained from the National Space Science Data Center. Other images taken of HD 207198 were of poorer quality so that summing images would not improve the signal-to-noise ratio. The equivalent widths were measured from the extracted spectrum supplied by NSSDC; no additional processing was performed.

### *b*) *Results*

The results from our observations toward stars in the Cep OB2 association are displayed in Tables 1 and 2. Table 1 compiles the molecular species, the spectroscopic notation for the transition, the *f*-value for the transition, and the results for HD 206267, HD 207198, and $\lambda$ Cep; the column densities derived from our measurements are shown in Table 2. No measurements of $C_2$ absorption toward 9 Cep were obtained because

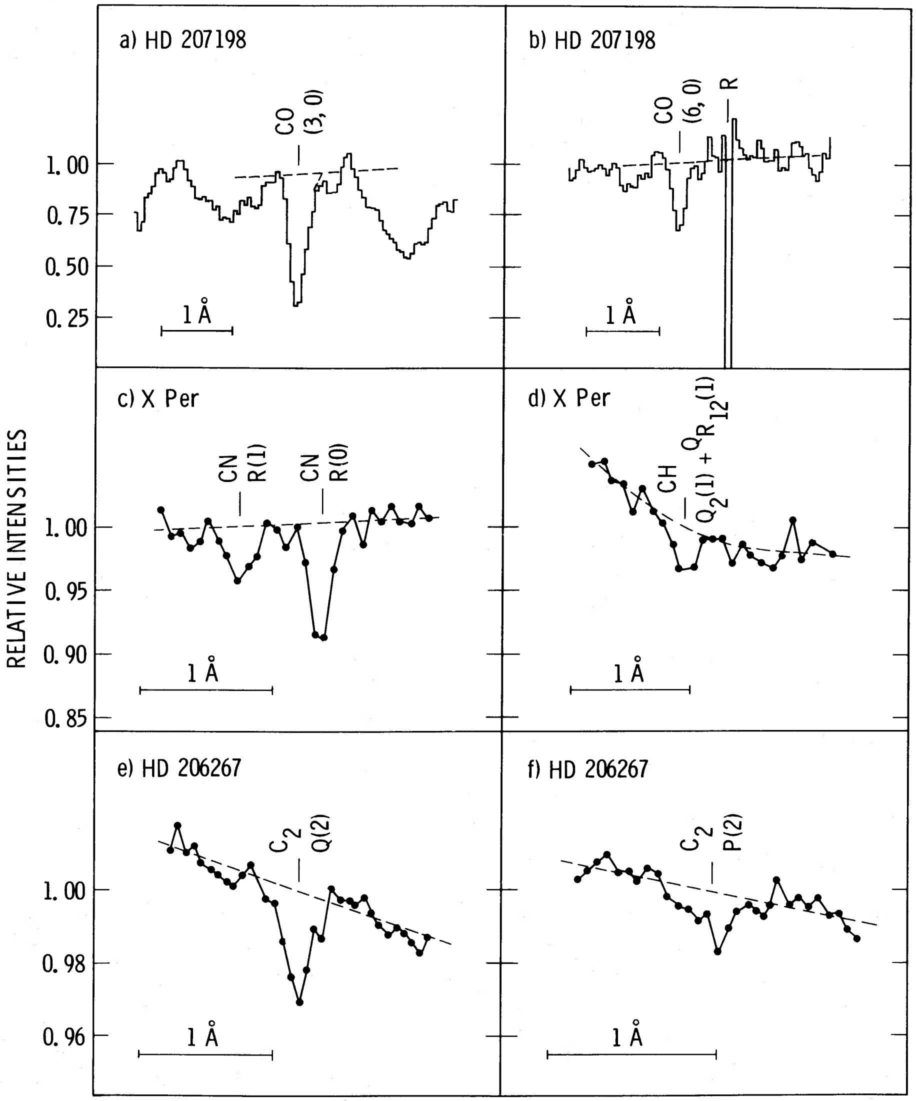

FIG. 1.—Sample spectra for various molecular features. The wavelength scale is indicated by the bar in each panel. The adopted continua are indicated by dashed lines. The " R " in (*b*) represents a reseau in the *IUE* image.

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TABLE 1

RESULTS FOR THE STARS IN THE CEPHEUS OB2 ASSOCIATION

| | | | $W_\lambda$(mÅ) | | |
|---|---|---|---|---|---|
| SPECIES | LINE | *f*-VALUE | HD 206267 | HD 207198 | λ Cep |
| $C_2$.......... | *R*(0) | 1.0(−3)[a] | 7.3 ± 1.0 | ≤6.1 | ≤3.6 |
| | *R*(2) | 4.0(−4) | ≤5.2 | ≤5.4 | ≤2.4 |
| | *Q*(2) | 5.0(−4) | 7.2 ± 1.2 | 3.8 ± 1.7 | ≤3.0 |
| | *P*(2) | 1.0(−4) | 2.9 ± 1.5 | ≤5.8 | ≤2.6 |
| | *R*(4) | 3.3(−4) | ... | ≤3.8 | ≤2.4 |
| | *Q*(4) | 5.0(−4) | 7.1 ± 2.3 | ≤6.2 | 1.9 ± 1.1 |
| | *P*(4) | 1.7(−4) | 2.6 ± 1.3 | ... | ... |
| | *Q*(6) | 5.0(−4) | 5.9 ± 1.7 | ≤3.6 | ≤2.4 |
| | *Q*(8) | 5.0(−4) | ≤2.0 | ... | ... |
| CO......... | (1–0) | 0.0343 | ... | 166 ± 9 | ... |
| | (2–0) | 0.0411 | ... | 130 ± 21 | ... |
| | (3–0) | 0.0360 | ... | 189 ± 18 | ... |
| | (4–0) | 0.0257 | ... | 115 ± 12 | ... |
| | (5–0) | 0.0161 | ... | 117 ± 27 | ... |
| | (6–0) | 0.0091 | ... | 54 ± 14 | ... |
| | (7–0) | 0.0048 | ... | 42 ± 8 | ... |

[a] 1.0(−3) = 1.0 × $10^{-3}$.

the expected equivalent widths were below our detection threshold of ~2 mÅ (see below). The errors in the measured equivalent widths were determined in a conservative manner by multiplying the root-mean-square deviation in the nearby continuum and the number of spectral elements across the wings of the line. Upper limits are listed when the measured equivalent width, which can be negative, is less than twice the error over the wavelength interval for a line. For $C_2$ all the lines are weak for a Doppler parameter of 1 km $s^{-1}$ so that the relationship

$$N(C_2) = \frac{W_\lambda(\text{mÅ})}{8.85 \times 10^{-21} \lambda(\text{Å})^2 f} \text{ cm}^{-2} \tag{1}$$

is applicable to the data of Table 1. Here, $W_\lambda$ is the equivalent width, $\lambda$ is the wavelength of the transition, and $f$ is the oscillator strength. The *f*-values are from Danks and Lambert (1983); recent laboratory experiments (cf. Davis *et al.* 1984; Bauer *et al.* 1986) indicate that the *f*-values are accurate to 20%. As expected, the results for *R*, *Q*, and *P* lines from the same rotational state, which have significantly different *f*-values, lead to similar values for the column density of the state. The CO data were analyzed with a profile-fitting program; the fitting procedure accounted for the rotational structure of the bands, which was not resolved by the instrumentation on *IUE*. The parameters adopted for the program included an excitation temperature of 4 K (Wannier, Penzias, and Jenkins 1982) and recently compiled *f*-values (van Dishoeck and Black 1986; E. F. van Dishoeck, private communication) based on the lifetime measurements of Field *et al.* (1983).

TABLE 2

MOLECULAR COLUMN DENSITIES FOR THE GAS TOWARD STARS IN CEPHEUS

| Species | Line | HD 206267 | HD 207198 | λ Cep |
|---|---|---|---|---|
| $C_2$.......... | *R*(0) | 1.1(13) | ≤9.0(12) | ≤5.3(12) |
| | *R*(2) | ≤1.9(13) | ≤2.0(13) | ≤8.8(12) |
| | *Q*(2) | 2.1(13) | 1.1(13) | ≤8.8(12) |
| | *P*(2) | 4.3(13) | ≤8.5(13) | ≤3.8(13) |
| | *R*(4) | ... | ≤1.7(13) | ≤1.1(13) |
| | *Q*(4) | 2.1(13) | ≤1.8(13) | 5.6(12) |
| | *P*(4) | 2.3(13) | ... | ... |
| | *Q*(6) | 1.7(13) | ≤1.1(13) | ≤7.1(12) |
| | *Q*(8) | ≤5.8(12)[a] | ... | ... |
| | Total | 7.6(13) | 3.0(13)[b] | 1.7(13)[b] |
| CO......... | Total | ... | 2.6(15) | 1.4(15)[c] |

[a] Separated *P*(4) and *Q*(8) by making results consistent with *Q*(4).

[b] Total $N(C_2)$ estimated by assuming $T_{rot}$ = 50 K; see text.

[c] Data from Tarafdar and Krishna Swamy 1984.

Joseph *et al.* (1986) analyzed the same ultraviolet data for the cloud toward HD 207198. Their equivalent widths and ours agree when the accuracy of the data are considered, except for the CO (2–0) band, where they measured an equivalent width almost twice as large as what we find. The factor of ~1.5 difference in column density between their work and ours arises primarily because of the different *f*-values used. The source for the *f*-values is not discussed in Joseph *et al.* (1986).

Table 3 shows the results for the cloud toward X Per. The second column lists the wavelength of the transitions and the line designation, the present results appear in the third column, and the fourth column lists the previous results. The last entry for each molecule is the column density we derive when a Doppler parameter of 1 km $s^{-1}$ is considered. The *f*-values applied to the data for CH are from Danks, Federman, and Lambert (1984) and for CN from Federman, Danks, and Lambert (1984). Our data for CH are more consistent with the CH λ4300 data of Frisch (1972) and Cohen (1973) than with the data of Lien (1984*a*) for λ3886. Moreover, our CN results agree with those of Clauser and Thaddeus (as quoted by Frisch 1972). It appears that Lien's optical results for CH λλ3886, 4300 are 2 times too large, suggesting an incorrect correction for background. Moreover, our results for the *R*(2) and *Q*(2) lines of $C_2$ are consistent with the upper limits quoted by Crutcher (as discussed in Lien 1984*b*).

The total column densities of $C_2$ for each of the directions are calculated under the assumption of an excitation temperature ($T_{ex}$) of 50 K. The expected column densities of $C_2$ for specific rotational lines observed as upper limits are consistent with this $T_{ex}$. For the considerable amount of data available for the cloud toward HD 206267, $T_{ex}$ of 50 K is derived; no evidence for optical pumping is seen for rotational levels with $J \leq 6$. If optical pumping were effective for higher lying levels, the column densities derived here would have to be increased approximately 20%–50% (cf. Danks and Lambert 1983; van Dishoeck and de Zeeuw 1984). This value for $T_{ex}$ is also assumed for the gas toward X Per because Lien (1984*b*) suggests such a value based on his detection of the *F–X* transition of $C_2$ at 1300 Å and a similar value of 70 K is obtained for the rotational temperature of $H_2$ (Mason *et al.* 1976). Our values for $N(C_2)$ indicate that $f_{00}$ is ~0.04 for the *F–X* transition; the derived $f_{00}$ compares favorably with the theoretical estimate of Pouilly *et al.* (1983).

The LSR velocities of the lines observed cannot be determined with great certainty but are consistent with previous measurements. The gas toward the stars in Cepheus probably has a velocity of about 0 km $s^{-1}$, the LSR velocity of atomic lines toward λ Cep (Hobbs 1974). The $C_2$ data are consistent with this velocity: Toward HD 206267 $v_{LSR} \approx -2 \pm 1$ km $s^{-1}$; toward HD 207198 $v_{LSR} \approx +2 \pm 2$ km $s^{-1}$; and toward λ Cep $v_{LSR} \approx 0$ km $s^{-1}$. The individual bands of CO seen toward HD 207198 have comparable offsets ($\lambda_{lab} - \lambda_{obs}$, where $\lambda_{obs}$ is the effective mean wavelength for the band) of ~0.1 Å from the wavelength scale of the extracted *IUE* spectrum, but a determination of $v_{LSR}$ from the CO data is not warranted because of

TABLE 3

RESULTS FOR X PERSEI

| SPECIES | LINE (Å) | | $W_\lambda$ (mÅ) This Work | $W_\lambda$ (mÅ) Previous Work | $N$(X) (cm$^{-2}$) |
|---|---|---|---|---|---|
| CH ............... | 4300.321 | $(2e + 2f)$ | ... | $15 \pm 6$[a]; $20 \pm 10$[b]; $33 \pm 3$[c] | 3.2(1.3) |
| | 3890.21 | $T_{2e}$ | $\leq 7.4$ | $7 \pm 3$[c] | $\leq$2.8(13) |
| | 3878.77 | $T_{2e}$ | $\leq 5.4$ | $\leq 6$[c] | ... |
| | 3886.41 | $T_{2f}$ | $6.1 \pm 2.6$ | $14 \pm 3$[c] | 1.5(13) |
| $N(\mathrm{CH})_{\mathrm{tot}}$ ........ | | | | | 3.0(13) |
| CN ............... | 3874.61 | $N'' = 0$ | $17.4 \pm 3.1$ | $18 \pm 3$[d] | 5.1(12) |
| | 3874.00 | $N'' = 1$ | $8.7 \pm 3.1$ | ... | 3.3(12) |
| | 3875.76 | $N'' = 1$ | $\leq 6.2$ | ... | $\leq$4.4(12) |
| $N(\mathrm{CN})_{\mathrm{tot}}$ ........ | | | | | 8.4(12) |
| $C_2$ | 8757.69 | $R(0)$ | $\leq 13.2$ | ... | $\leq$1.9(13) |
| | 8753.95 | $R(2)$ | $\leq 13.2$ | $\leq 5$[e] | $\leq$4.9(13) |
| | 8761.19 | $Q(2)$ | $6.7 \pm 3.5$ | $\leq 5$[e] | 2.0(13) |
| | 8763.75 | $Q(4)$ | $\leq 9.2$ | ... | $\leq$2.7(13) |
| $N(\mathrm{C_2})_{\mathrm{tot}}$ ........ | | | | | 5.3(13)[f] |

[a] Frish 1972.

[b] Cohen 1973.

[c] Lien 1984*a*.

[d] Clauser and Thaddeus as quoted by Frisch 1972.

[e] Crutcher, as quoted by Lien 1984*b*.

[f] Based on $T_{\mathrm{ex}} = 50$ K.

the limited spectral resolution. The CH and CN data presented here toward X Per indicate that $v_{\mathrm{LSR}}$ for this direction is $+4.0 \pm 1.5$ km s$^{-1}$; previous results (Dickman *et al.* 1983) indicate $v_{\mathrm{LSR}} \approx +6$ km s$^{-1}$.

## III. ANALYSIS

The newly acquired molecular data are first discussed in terms of the framework outlined by Federman, Danks, and Lambert (1984). They studied the chemistry of CN under steady state conditions and found that the main production routes for CN are through reactions involving atomic nitrogen and the *neutral* molecules CH and $C_2$. When local densities and column densities are considered equivalent, $N$(CN) is related to $N$(CH) and $N(C_2)$. In particular,

$$N(\mathrm{CN}) = \frac{[N(\mathrm{C_2}) + 0.4N(\mathrm{CH})]k_1 x(\mathrm{N})n}{G_0(\mathrm{CN}) \exp(-\tau_{\mathrm{uv}}) + k_2 x(\mathrm{O})n} \ \mathrm{cm}^{-2} , \qquad (2)$$

where $k_1$ and $k_2$ are the rate constants for the reactions $C_2 + N \rightarrow CN + C$ and $CN + O \rightarrow CO + N$, respectively; $x$(N) and $x$(O) are the abundances of N and O; $G_0$(CN) is the photodestruction rate of CN; $\tau_{\mathrm{uv}}$ is the optical depth at the wavelength for dissociation: and $n$ is the gas density. The rate constants have a temperature dependence of the form $(T/300)^{0.5}$. Of the parameters in equation (2), only the rate constant for $C_2 + N$ and the CN photodissociation rate have not been determined through laboratory measurements.

Table 4 shows the comparison between the observed and the analytical results for $N$(CN) toward all the directions for which the three molecules are detected. This table is an updated version of the results presented in Table 2 of Federman, Danks, and Lambert (1984); the differences between the two tables include a measured column density determined with a Doppler parameter of 1 km s$^{-1}$, an increased nitrogen abundance of $6.9 \times 10^{-5}$ (Hibbert, Dufton, and Keenan 1985), and an enhanced photodestruction rate of $1 \times 10^{-10}$ s$^{-1}$. The values for $k_1$ and $k_2$ at 300 K remain the same at $5 \times 10^{-11}$

TABLE 4

COMPARISON OF OBSERVED AND PREDICTED $N$(CN)

| STAR | $n$ (cm$^{-3}$) | $T$ (K) | $\tau_{\mathrm{uv}}$ | $N$(CH) (cm$^{-2}$) | $N(C_2)$ (cm$^{-2}$) | $N$(CN) (cm$^{-2}$) Observed | $N$(CN) (cm$^{-2}$) Predicted | Observed/ Predicted |
|---|---|---|---|---|---|---|---|---|
| $o$ Per ............. | 500 | 50 | 1.86 | 1.3(13) | 2.7(13) | 2.6(12) | 1.3(12) | 2.0 |
| $\zeta$ Per ............. | 400 | 30 | 2.05 | 2.2(13) | 3.5(13) | 3.9(12) | 1.4(12) | 2.8 |
| X Per ............. | 1000 | 25 | 3.84 | 3.1(13) | 5.3(13) | 8.4(12) | 1.6(13) | 0.5 |
| HD 29647 ........ | 1500 | 10 | 6.76 | 1.6(14) | 1.5(14) | 1.6(14) | 1.1(14) | 1.4 |
| HD 147889 ....... | 1000 | 25 | 6.76 | 1.2(14) | 1.2(14) | 3.5(13) | 8.4(13) | 0.4 |
| $\rho$ Oph A .......... | 500 | 45 | 2.91 | 2.4(13) | 2.6(13) | 2.0(12) | 3.6(12) | 0.6 |
| $\chi$ Oph ............ | 400 | 45 | 3.29 | 3.4(13) | 3.5(13) | 1.3(12) | 5.5(12) | 0.2 |
| $\zeta$ Oph ............ | 700 | 30 | 1.98 | 2.5(13) | 2.2(13) | 2.6(12) | 1.6(12) | 1.6 |
| HD 154368 ....... | 400 | 25 | 5.39 | 8.7(13) | 2.6(13) | 2.6(13) | 2.8(13) | 0.9 |
| HD 206267 ....... | 500 | 40 | 3.16 | 2.6(13) | 7.6(13) | 1.0(13) | 1.0(13) | 1.0 |
| HD 207198 ....... | 500 | 40 | 3.78 | 4.5(13) | 3.0(13) | 5.7(13) | 8.7(13) | 0.6 |
| $\lambda$ Cep ............ | 500 | 40 | 3.47 | 2.2(13) | 1.7(13) | 2.4(12) | 3.8(12) | 0.6 |

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$cm^3\ s^{-1}$ and $1.8 \times 10^{-11}\ cm^3\ s^{-1}$; the oxygen abundance is $3.5 \times 10^{-4}$. The measurements of CH and CN for HD 147889 are from Cardelli and Wallerstein (1986), which are more comprehensive than those of Crutcher and Chu (1985), and for the stars in Cepheus are from Chaffee and Dunham (1979). It should be noted that for the two lines in common, the equivalent widths from Cardelli and Wallerstein are larger by up to a factor of 3 than the equivalent widths from Crutcher and Chu. The $C_2$ data for HD 147889 are from van Dishoeck and de Zeeuw (1984). The references to the other previously published data are found in Federman, Danks, and Lambert (1984). The gas densities, $n(\text{H I}) + 2n(H_2)$, temperatures, and $\tau_{uv}$ used in the present analysis are indicated in Table 4. The slight changes in $n$ and $T$ for $o$ Per, $\zeta$ Per, $\chi$ Oph, and $\zeta$ Oph from the previous analysis are due to the recent work of van Dishoeck and Black (1986). For the gas toward the stars in Cepheus, the values used for $n$ and $T$ are 500 $cm^{-3}$ and 40 K; for X Per and HD 147889, where the lines of sight pass through more interstellar material, the values are 1000 $cm^{-3}$ and 25 K. For HD 147889, the result with $T \approx 60$ K, as suggested by van Dishoeck and de Zeeuw (1984), differs by less than 5% from that in Table 4. The density and temperature for the other directions are the same as those used by Federman, Danks, and Lambert (1984). $\tau_{uv}$ is again taken to be $2A_V$; this is equivalent to taking $\tau_{uv} \approx 4\tau_V$ (cf. Code *et al.* 1976) from the edge of the model cloud to its center.

The analytical results for $N$(CN) based on equation (2) are within a factor of 2–3 of the observed values. The results from Federman, Danks, and Lambert (1984) are altered slightly because a larger value for $N$(CH) based on a Doppler parameter of 1 km $s^{-1}$ was used in the present analysis, and because the ratio of $x$(N) to $G_0$(CN) is now taken to be $6.9 \times 10^5$ s as opposed to $9.0 \times 10^5$ s. For the directions where the predicted values are larger than the measured values ($\chi$ Oph and HD 147889), a higher flux of dissociating radiation may be needed; van Dishoeck and Black (1986) required that the UV flux in the cloud toward $\chi$ Oph be the highest of the directions they modeled. Moreover, the CN results for HD 147648 of Cardelli and Wallerstein (1986) indicate less CN for the amount of observed CH (see below). HD 147648, HD 147889, and $\chi$ Oph are associated with the $\rho$ Ophiuchi cloud complex, and the results for these three lines of sight suggest an enhanced UV field for the whole region.

The compilation presented in Table 4 bears on the analysis of van Dishoeck and Black (1986). They concluded that the neutral-neutral reactions were of minor importance for the production of CN, contrary to the results of Viala (1986) and us. Federman, Danks, and Lambert (1984) showed that reactions involving NH and $C^+$ with the upper limit of Crutcher and Watson (1976) for NH and involving $CH^+$ and N with the observed amount of $CH^+$, which is significantly underestimated in steady state models, produce less than 50% of the CN. One main difference in the chemical schemes arises from their matching the observed amount of $N(C_2)$ based on theoretical $f$-values. This reduces the value for $N(C_2)$ by roughly a factor of 2 and, hence, the calculated value for $N$(CN) by a similar factor. The predictions based on the model of van Dishoeck and Black, when the experimental $f$-values for $C_2$ are used, are within 50% of the observed values for $N(C_2)$ and $N$(CN). The remaining differences are attributed to the values used for the photodissociation rate of CN in the two calculations. An advantage in our analytical approach for $N$(CN) is that the effects of uncertain rates, especially photodissociation rates, are minimized through the use of observed values for the intermediates.

Since equation (2) reproduces the data for lines of sight passing through clouds where photochemistry dominates (e.g., the stars in the Cep OB2 association) and where chemical reactions dominate (e.g., HD 29647), we can invert the equation and solve for the expected column density of $C_2$ toward 9 Cep. For this direction $N$(CH) is $2.8 \times 10^{13}\ cm^{-2}$ and $N$(CN) is $\leq 1.7 \times 10^{12}\ cm^{-2}$ (from the data of Chaffee and Dunham 1979). The predicted value of $N(C_2)$ toward 9 Cep is $\leq 7 \times 10^{12}\ cm^{-2}$. Note that the amount of CH is comparable to the other directions studied in Cepheus, but $N$(CN) is less. When $T_{ex}$ is 50 K and when the high-lying rotational levels are populated via optical pumping, approximately one-quarter of the $C_2$ molecules are in the $J = 2$ state. Therefore, the equivalent width of the strong $Q(2)$ line is less than 1 mÅ, which is below our detection limit. The gas toward the Cep OB2 association is probably much closer to 9 Cep than the other stars, allowing more dissociating radiation to penetrate the cloud in this sightline.

In our previous work, we investigated the chemistry of CO, CH, and CN by plotting $N$(X) against $N(H_2)$. For many moderately reddened lines of sight, however, no direct measurement of $H_2$ is available and an alternative means of analysis is necessary. Federman (1982) and Danks, Federman, and Lambert (1984) showed that $N$(CH) varied linearly with $N(H_2)$ for $N(\text{CH}) \leq 2\text{–}3 \times 10^{13}\ cm^{-2}$. Cardelli and Wallerstein (1986) estimated $N(H_2)$ for moderately reddened directions from $E(B-V)$ and the relationship between $E(B-V)$ and $N(H_2)$ derived by Bohlin, Savage, and Drake (1978). They found that the linear relationship between $N$(CH) and $N(H_2)$ continues for $N(\text{CH}) \approx 10^{14}\ cm^{-2}$. Most recently, Mattila (1986) measured the 9 cm emission from CH in dark clouds and concluded that the relationship between the two molecules persisted until $A_v \approx 4$ mag $[N(H_2) \sim 4 \times 10^{21}\ cm^{-2}]$, where $N$(CH) reaches a maximum value of $\sim 10^{14}\ cm^{-2}$. Mattila suggested that since the extinction through dark clouds was greater than 4 mag, the CH emission arose from the envelope of the cloud. Because of the correspondence between $N$(CH) and $N(H_2)$, $N$(CH) is used in place of $N(H_2)$ in the analysis presented below.

In addition to the constancy of the slope between $N$(CH) and $N(H_2)$, the trend seen in the data of Federman (1982), Danks, Federman and Lambert (1984), Cardelli and Wallerstein (1986), and Mattila (1986) is continuous, i.e., the ratio between $N$(CH) and $N(H_2)$ is constant for the different data sets for CH. The steady state rate equation for CH is

$$N(\text{CH}) = \frac{0.67k_5\, n(C^+)N(H_2)}{G(\text{CH}) + k_3\, n(C^+)}\ \text{cm}^{-2} \tag{3}$$

in the notation of Federman (1982). $k_5$ ($5 \times 10^{-16}\ cm^3\ s^{-1}$) is the rate constant for radiative association between $C^+$ and $H_2$; $k_3$ ($10^{-9}\ cm^3\ s^{-1}$) is the rate constant for the reaction of $C^+ + CH \rightarrow C_2H^+ + H$; $n(C^+)$ is the local density of $C^+$ and equals $2.5 \times 10^{-4}n$; and $G$(CH) $[1.3 \times 10^{-9} \exp(-\tau_{uv})\ s^{-1}]$ is the photodissociation rate for CH including attentuation. The abundance for $C^+$ of $2.5 \times 10^{-4}$ is based on the assumptions that each carbon atom is singly ionized in diffuse clouds and that carbon is depleted by a factor of 2. For $N(\text{CH}) \leq 3 \times 10^{13}\ cm^{-2}$, the ratio of $N$(CH) to $N(H_2)$ is reproduced for densities of a few hundred particles per cubic centimeter $[n(C^+) \approx 8 \times 10^{-2}\ cm^{-3}]$. For clouds with larger values of $N$(CH), where $N(H_2)$ is inferred from $A_V$, the use of this value for $n(C^+)$ predicts ratios that are factors of 5–10 larger than are observed. This can be reconciled by reducing the amount of $C^+$ in the moderately reddened directions by a similar

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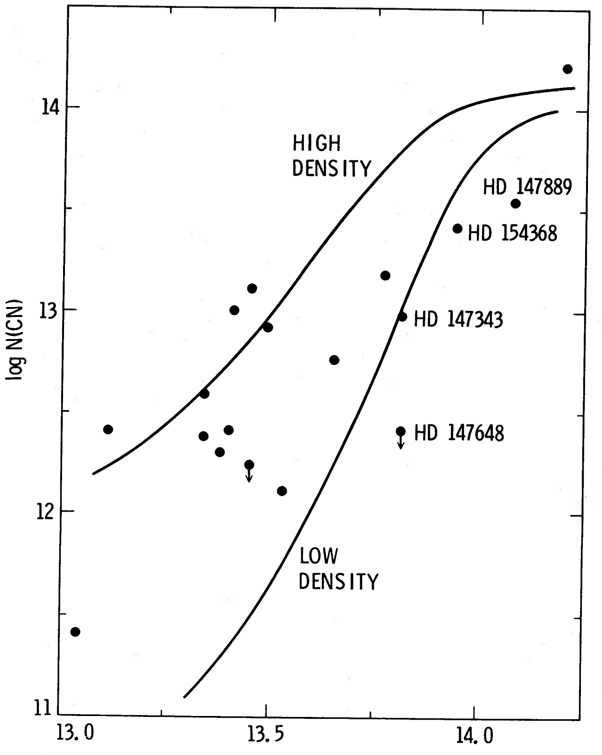

FIG. 2.—A log-log plot of $N$(CH) vs. $N$(CN). The two curves illustrate the results of the chemical models discussed in the text.

factor. Thus *for moderately reddened lines of sight* [$E(B-V) \approx 0.7$ *mag*], *the carbon balance is seen to shift from ionized carbon to neutral forms of gas phase carbon*, as predicted by Glassgold and Langer (1975).

Figures 2 and 3, respectively, show the available data for $N$(CN) and $N(C_2)$ plotted against $N$(CH). For clarity, upper limits with log $N$(CN) < 11.50 are not shown. The specific directions, where significant differences (greater than a factor of 3) from the general trends are apparent, are indicated.

As first noted by Cardelli and Wallerstein (1986), a change in slope may be present at $N(CH) \approx 5 \times 10^{13}$ cm$^{-2}$ when $N$(CN) is plotted against $N$(CH) (fig. 2). Directions with smaller amounts of $N$(CH) show a cubic variation between $N$(CN) and $N$(CH). When the upper limits presented by Federman, Danks, and Lambert (1984) are included in an analysis of censored data (cf. Isobe, Feigelson, and Nelson 1986) for the sample, the slope of 3 is preserved. For directions with larger amounts of CH a linear relationship seems to represent the data better. The possible change in slope that appears in the available data could be ascribed to different chemical regimes: A cubic relationship would arise in a photochemical regime (cf. Federman, Danks, and Lambert 1984), while a linear relationship would correspond to the regime where chemical reactions dominate.

Such a result could be understood with reference to equation (2). The two terms in the denominator of the equation are equal when $\tau_{uv}$ is about 4; this optical depth is equivalent to 2 mag of extinction through the cloud. From the relationship $N(CH)/A_V = 2 \times 10^{13}$ cm$^{-2}$ mag$^{-1}$ (Federman 1982), the two destruction terms for CN are equal at $N(CH) \approx 4 \times 10^{13}$ cm$^{-2}$. Moreover, when chemical reactions are the primary means of destroying neutral molecules, $N$(CN) and $N(C_2)$ are proportional to $N$(CH) because of cancelation of the density dependent terms in the rate equations for CN and $C_2$. The corresponding equation for $N(C_2)$ is

$$N(C_2) = \frac{k_3 n(C^+) N(CH)}{G(C_2) + k' n(O)} \text{ cm}^{-2} \qquad (4)$$

(cf. Federman, Danks, and Lambert 1984), where $n(O) = x(O)n$, and $k' = 4 \times 10^{-11}(T/300)^{0.5}$ cm$^3$ s$^{-1}$. Thus *chemical reactions dominate the destruction of* CN *for* $N(CH) > 4 \times 10^{13}$ cm$^{-2}$ *and a linear trend is expected between* $N$(CN) *and* $N$(CH) *in this regime.*

A change in slope at a similar value of $N$(CH) may also be present in the graph of $N(C_2)$ versus $N$(CH), as shown in Figure 3. The data are too sparse, however, to state definitively that a change occurs. An analysis of the rate equation for $C_2$ in terms of $N(C_2)$ (eq. [4]) indicates that a break in the curve should occur at $N(CH) \approx 4$–$5 \times 10^{13}$ cm$^{-2}$. For $C_2$ the photochemical regime has a slope of 2 (cf. Federman, Danks, and Lambert 1984) and the chemical regime again has a slope of 1. More data, especially for directions with $N$(CH) of 4–8 × $10^{13}$ cm$^{-2}$, are needed to verify the anticipated trends.

Also displayed in Figures 2 and 3 are theoretical curves based on the analytic expressions for $N$(CN) and $N(C_2)$. Two constant density, constant temperature calculations were performed so that a clearer understanding of the transition could be acquired: one with $n = 150$ cm$^{-3}$ and $T = 50$ K and the other with $n = 1500$ cm$^{-3}$ and $T = 25$ K. Such values for $n$ and $T$ span the values deduced from observational data and chemical models. The optical depth needed for the photodissociation rates was derived from the correspondence between $N$(CH) and $A_V$ discussed above. A variation in the abundance of $C^+$ was necessary before reasonable agreement could be obtained between the model and the data for $N$(CN) and $N(C_2)$ as a function of $N$(CH) for lines of sight with

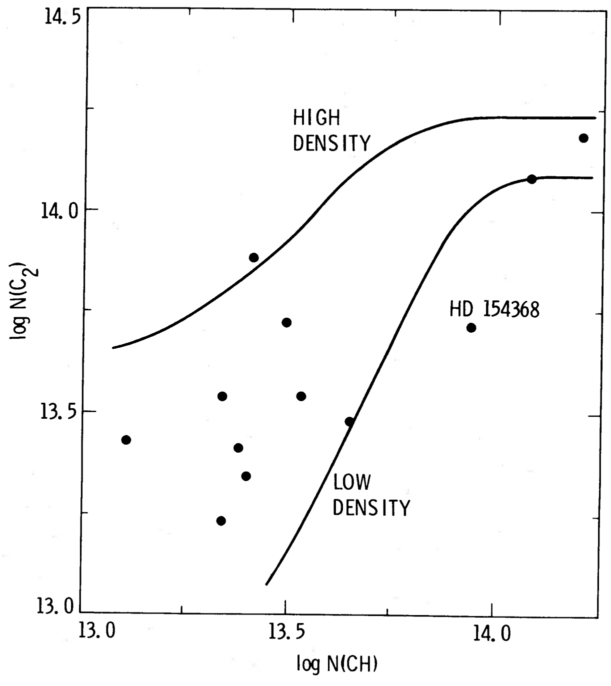

FIG. 3.—Same as Fig. 2 for log $N(C_2)$ vs. log $N$(CH)

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$N(CH) > 6 \times 10^{13}$ cm$^{-2}$. The curves in Figures 2 and 3 include a linear decrease in the abundance of $C^+$ to a factor 1/15 the initial abundance ($2.5 \times 10^{-4}$). The main effect of the variation in $x(C^+)$ is the leveling off of the curves for directions with the largest amounts of CH. The decrease in the abundance of $C^+$ is expected for the directions with $A_V > 2$ mag because $C^+$ is becoming neutralized through reactions leading to C and CO (Glassgold and Langer 1975). Thus, both the ratio of $N(CH)$ to $N(H_2)$ and the chemistries of CN and $C_2$ require the decrease in $x(C^+)$.

The calculations span the data, indicating that most of the clouds studied have physical conditions lying between the two calculations. These results are consistent with the more comprehensive chemical treatment for clouds of low reddening ($A_V \leq 1$ mag) by Danks, Federman, and Lambert (1984) for CH versus $H_2$ and by Federman, Danks, and Lambert (1984) for CN versus $H_2$. Several directions, predominantly in the vicinity of the $\rho$ Ophiuchi Molecular Cloud, have values for $N(CN)$ below the low-density curve. The probable reason for the low values of $N(CN)$ toward these lines of sight is enhanced photodissociation, as discussed above with respect to Table 4.

The available ultraviolet results for $N(CO)$ are presented in Figure 4. The radio data toward HD 29647 and HD 147889 are not included because of the possibility of contamination from dense clumps in the larger radio beam. For most of the lines of sight observed in the $A$–$X$ bands of CO, a Doppler parameter of $\sim 1$ km s$^{-1}$, derived from the profile fitting, and $T_{ex}$ of 4 K, are used in obtaining $N(CO)$. Such an analysis increases the derived value for $N(CO)$ over that for a curve-of-growth analysis by at most a factor of $\sim 2$ for directions with $N(CH) \approx 10^{13}$ cm$^{-2}$. The available data are not always precise enough to yield a self-consistent determination for $N(CO)$ for all the measured bands; our analysis gave more weight to weaker bands (3–0, 4–0, etc.). The results for $o$ Per and $\zeta$ Per have been increased also by a factor of $\sim 2$ over the results of Snow (1975, 1977), who fitted the profile of the $B$–$X$ transition, because we used $f_{B-X} = 0.0052$ (cf. Krishnakumar and Srivastava 1986) in the analysis. A similar increase occurs when the data for $\chi$ Oph of Frisch (1980) is analyzed with an $f$-value of 0.089 for the $C$–$X$ transition, the value adopted by Federman *et al.* (1980). The directions with $N(CH) \leq 5 \times 10^{12}$ cm$^{-2}$ are not significantly affected when the thin-line approximation is used to derive $N(CO)$.

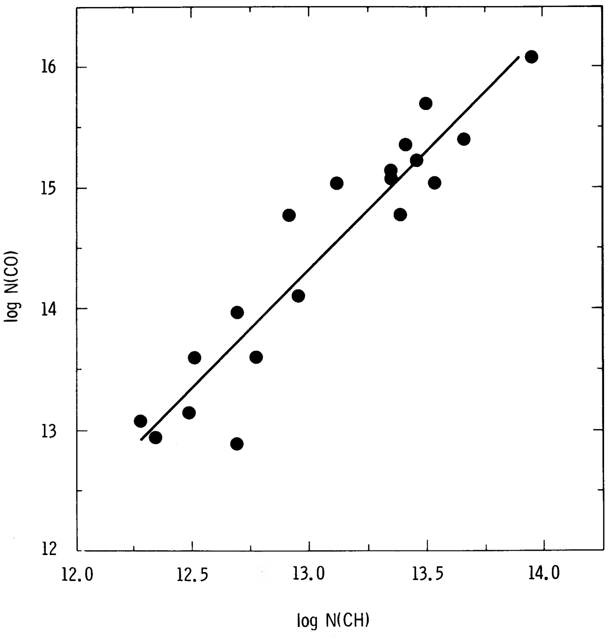

FIG. 4.—A plot of log $N(CO)$ against log $N(CH)$. A least-squares fit to the data is shown by the line, which has a slope of 1.97.

Federman *et al.* (1980) found a quadratic variation between $N(CO)$ and $N(H_2)$, and a similar variation arises when $N(CO)$ is plotted against $N(CH)$. The approximately quadratic relationship ($m = 1.97$) continues for directions (HD 154368) with $N(CH) \approx 10^{14}$ cm$^{-2}$, but the lack of CO data for other similar directions lessens the importance of this fact. One interesting result of the CO plot is that there is no apparent sharp increase in slope, as would be expected if self-shielding of CO from photodissociation through line absorption were playing a dominant role in the chemistry.

### IV. CONCLUDING REMARKS

New data of $C_2$ toward X Per, HD 206267, HD 207198, and $\lambda$ Cep, of CH and CN toward X Per, and of CO toward HD 207198 have been obtained. The column densities of CH, $C_2$, CN, and CO toward the stars in the Cepheus OB2 association are similar to reddened directions in Perseus ($o$ Per and $\zeta$ Per) and in Ophiuchus ($\rho$ Oph, $\chi$ Oph, and $\zeta$ Oph), indicating a similarity in physical conditions for the foreground clouds. The differences, especially in $N(CN)$, are ascribed to enhanced dissociating radiation. The molecules CH and $C_2$ are less affected by the radiation because they are formed at earlier stages in the chemical sequence than is CN (see Federman, Danks, and Lambert 1984). Slightly larger column densities are present in the gas in front of X Per.

The available data for other directions, including directions with $E(B-V)$ as large as 1.0 mag, have been analyzed in a self-consistent manner by using a uniform set of $f$-values and by using a Doppler parameter of 1 km s$^{-1}$. The combined set of data has been applied to the study of the transition from a photochemical regime to a chemical regime. For the sightlines with detections of CH, $C_2$, and CN, the measured value of $N(CN)$ has been compared to the analytical expression (eq. [2]) described by Federman, Danks, and Lambert (1984). The observed and predicted values for $N(CN)$ agree to within a factor of 2–3, even though some of the directions sample gas dominated by photochemistry while others sample gas dominated by chemical reactions.

The data for $N(CN)$, $N(C_2)$, and $N(CO)$ have been plotted against $N(CH)$ in order to elucidate the chemistry of carbon-bearing molecules more clearly. The column density of $N(CH)$ has been used in the present analysis because many of the moderately reddened directions do not have data for $N(H_2)$ and because of the linear relationship between $N(CH)$ and $N(H_2)$ for clouds with $A_v \leq 4$ mag (Cardelli and Wallerstein 1986; Mattila 1986). The observed trends for CN and $C_2$ suggest a change in slope at $N(CH) \approx 5 \times 10^{13}$ cm$^{-2}$. Below this value for $N(CH)$, photodestruction is predicted to dominate and the slope is determined by the photochemistry (see Federman, Danks, and Lambert 1984). For directions with more $N(CH)$, a linear correlation, which is consistent with destruction occurring through chemical reactions, is expected. More data toward lines of sight with $N(CH) \sim 4$–$8 \times 10^{13}$ cm$^{-2}$ are needed to substantiate the present findings. Furthermore, the continuous trend between $N(CH)$ and $N(H_2)$ for directions with $N(CH)$ as large as $10^{14}$ cm$^{-2}$ and the chemical

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models for $N(\mathrm{CN})$ and $N(\mathrm{C_2})$ indicate that carbon is mostly in the form of neutral species in moderately reddened clouds; some of the required decrease in the $\mathrm{C^+}$ abundance may be the effect of enhanced depletions in these clouds.

The CO results show that the effects of self-shielding are more subtle than previously believed. An analysis based on profile-fitting increases $N(\mathrm{CO})$ by a factor of $\sim 2$ for directions with $N(\mathrm{CH}) \geq 10^{13}$ cm$^{-2}$. A quadratic dependence between CO and CH is seen, suggesting that photochemistry dominates the destruction of CO for the lines of sight so far studied by ultraviolet transitions. More data of high precision for CO toward moderately reddened directions is needed, however, before quantifiable statements regarding the CO chemistry can be made. Results with the High Resolution Spectrometer on the Hubble Space Telescope are likely to elucidate the CO chemistry in these clouds.

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