

MODELING THE CHEMISTRY OF DENSE INTERSTELLAR CLOUDS. I.  
OBSERVATIONAL CONSTRAINTS FOR THE CHEMISTRYS. R. FEDERMAN,<sup>1,2</sup> W. T. HUNTRESS, JR.,<sup>1</sup> AND S. S. PRASAD<sup>1,3</sup>*Received 1989 March 27; accepted 1989 November 15*

## ABSTRACT

A search for correlations arising from molecular line data has been made in order to place constraints on the chemical models of interstellar clouds. Observations of CO, H<sub>2</sub>CO, NH<sub>3</sub>, HC<sub>3</sub>N, HC<sub>5</sub>N, and several other species have been compiled. The column density of H<sub>2</sub> has been obtained from determinations of  $A_V$ . At  $10^{21}$  H<sub>2</sub> cm<sup>-2</sup>,  $N(\text{CO})$  for dark clouds is a factor of 6 greater than the value for diffuse clouds. This result implies that the strength of the UV radiation field where CO shields itself from dissociation is approximately one-half the strength of the average Galactic field. Also, the dark cloud data indicate that the abundance of CO continues to increase with  $A_V$  for directions with  $A_V \leq 4$  mag, although less steeply with  $N(\text{H}_2)$  than is the case for diffuse clouds. For H<sub>2</sub>CO, a quadratic relationship is obtained in plots versus H<sub>2</sub> column density. The data suggest a possible turnover at the highest values for  $A_V$  ( $\geq 4-5$  mag). Ammonia shows no correlation with H<sub>2</sub>, C<sup>18</sup>O, HC<sub>3</sub>N, or HC<sub>5</sub>N, in part because for dark clouds the column density of NH<sub>3</sub> is nearly constant at  $10^{15}$  cm<sup>-2</sup>. A strong correlation is found between HC<sub>5</sub>N and HC<sub>3</sub>N, indicating the chemical link between the cyanopolyynes. Possible trends are also exhibited in plots of the cyanopolyynes versus C<sub>4</sub>H, but the weak correspondences with C<sup>18</sup>O suggest that emission from the cyanopolyynes and C<sup>18</sup>O arises in separate regions.

*Subject headings:* interstellar: molecules — molecular processes

## I. INTRODUCTION

Column densities are the basic observational data in studies of interstellar molecules. Correlations among the observed column densities  $N(X)$  of molecular species X are therefore very valuable in constraining theoretical chemical or chemical-dynamical models of interstellar molecular clouds. Equation (1),

$$N(A) = a[N(B)]^b, \quad (1)$$

represents a simple, yet broad-based correlation. The constants  $a$  and  $b$  in equation (1) are expected to be governed by chemical kinetics and by the physical structure of the cloud. For chemically unrelated species, the exponent helps to determine spatial correspondences within the cloud. For instance, Federman and collaborators (Federman, Danks, and Lambert 1984; Federman and Lambert 1988) argued that a value of 1 for  $b$  in the case of  $A = \text{CH}$  and  $B = \text{H}_2$  implies that the chemistry of the CH molecule does not involve any neutral precursor species. Given the difficulties involved in the minimization process for nonlinear, least-squares fitting, the constants  $a$  and  $b$  in equation (1) are derived most easily from a linearized expression:

$$\log N(A) = \log a + b \log N(B). \quad (2)$$

Throughout this paper, therefore, we work in the logarithmic domain and concentrate our efforts on observations of dark clouds. We present plots of  $\log N(X)$ , where X is H<sub>2</sub>, CO, H<sub>2</sub>CO, NH<sub>3</sub>, HC<sub>3</sub>N, HC<sub>5</sub>N, and C<sub>4</sub>H, and values of  $a$  and  $b$  whenever physically reasonable.

Correlations among molecular species observed in dark clouds have been sought in the past (e.g., Frerking, Langer and

Wilson 1982; Benson and Myers 1983; Churchwell, Nash, and Walmsley 1984; Millar and Freeman 1984a; Cernicharo and Guelin 1987). Several studies have displayed results on graphs with linear axes, a technique that has disadvantages. Most important, it leads one to seek relationships of the form

$$N(A) = \alpha + \beta N(B). \quad (3)$$

Such relationships do not satisfy the asymptotic boundary condition that  $N(A) \rightarrow 0$  when  $N(B = \text{H}_2) \rightarrow 0$ . Allowance for  $\alpha \equiv 0$  makes equation (3) a special case of equation (1) with  $b$  equal to 1. The present work also builds upon the previous logarithmic analyses by incorporating more data and more species in the analysis.

A discussion of the compiled data appears in the next section (§ II). Our results for oxygen-bearing and nitrogen-bearing species are described in §§ III and IV, respectively. This breakdown is partly due to the fact that our compilations for CO and H<sub>2</sub>CO apply to the outer regions ( $A_V \leq 4$  mag) of dark clouds, while the results for NH<sub>3</sub>, HC<sub>3</sub>N, HC<sub>5</sub>N, and several carbon-chain molecules apply predominantly to the cores ( $A_V \geq 4$  mag) of dark clouds. For cloud cores, extinction measurements represent lower limits, and comparisons involving species other than H<sub>2</sub> are more meaningful. Data on C<sup>18</sup>O are used in analyzing the correlation of CO with H<sub>2</sub>. Detailed interpretation of the physical significance of the derived values of  $a$  and  $b$  are beyond the scope of this empirical paper. However, we make an exception in the case of CO because of the timeliness of our results in light of recent strides made in the modeling of CO self-shielding (e.g., van Dishoeck and Black 1988). The final section, § V, presents our conclusions.

## II. THE MOLECULAR DATA

The molecular data for dark clouds are compiled from measurements that are available in the literature. The sources for our compilation are given in Table 1. Several constraints are

<sup>1</sup> Jet Propulsion Laboratory, California Institute of Technology.

<sup>2</sup> Department of Physics and Astronomy, The University of Toledo.

<sup>3</sup> Departments of Physics and Astronomy, University of Southern California.

applied to the compilation so that a self-consistent approach is obtained. Foremost, we do not consider data from clouds with substantial amounts of massive star formation, including the  $\rho$  Oph Cloud, because of its effects on the chemistry in the cloud. Second, we restrict ourselves to measurements for directions with  $1 \text{ mag} < A_V < \sim 5 \text{ mag}$ . The lower limit is necessary to ensure that the typical telescope beam ( $\sim 2'$ ) does not inadvertently sample a dense clump near an unreddened sightline; the rough upper limit is required only for correlations between the molecule of interest and  $A_V$  [or equivalently  $N(\text{H}_2)$ ]. Other comparisons for cores of clouds are possible. Third, several commonly observed species, such as HCN and  $\text{HCO}^+$ , are not included in the compilation because of severe saturation in the measured transitions for the main isotopic species. Fourth, not all of the available references are suitable for our study. Only those studies for which a specific value for the parameters of interest [ $N(X)$  or  $\int T_L dv$ , where  $T_L$  is the line temperature] is obtainable without interpolation are utilized. Results presented only in the form of contour plots are not used. Although contour maps are quite useful for displaying similarities and differences in molecular distributions, they are less useful for the necessary direct comparisons needed in chemical modeling. Fifth, to obtain reasonable statistics, we analyze those data on a limited number of species that have more than 10 entries. Last, we obtain  $N(X)$  for a given species at a specific position by averaging different sets of measurements after converting to the same set of excitation parameters. The fourth and last points are discussed in more detail below.

TABLE 1  
REFERENCE FOR OBSERVATIONS

Molecule	References
Diffuse Clouds <sup>a</sup>	
CO .....	1, 2, 3
Dark Clouds	
CO .....	4, 5, 6, 7, 8
H <sub>2</sub> CO .....	9, 10, 11, 12, 13
NH <sub>3</sub> .....	14, 15, 16, 17
HC <sub>3</sub> N .....	15, 16, 18, 19, 20
HC <sub>5</sub> N .....	14, 15, 19
C <sub>4</sub> H .....	15, 21

<sup>a</sup> The UV data are results based on fitting profiles with unresolved structure to the absorption lines (Federman and Lambert 1988).

REFERENCES.—(1) Federman *et al.* 1980; (2) Tarafdar and Krishna Swamy 1982; (3) Federman and Lambert 1988; (4) Baudry *et al.* 1981; (5) Myers, Linke, and Benson 1983; (6) Ungerer *et al.* 1985; (7) Duvert, Cernicharo, and Baudry 1986; (8) Cernicharo and Guelin 1987; (9) Minn and Greenberg 1979; (10) Sherwood and Wilson 1981; (11) Cohen *et al.* 1983; (12) Pöppel, Rohlfs, and Celnik 1983; (13) Minn and Greenberg 1987; (14) Benson and Myers 1983; (15) Cernicharo, Guelin, and Askne 1984; (16) Churchwell, Nash, and Walmsley 1984; (17) Gaida, Ungerechts, and Winnewisser 1984; (18) Bujarrabal *et al.* 1981; (19) Tölle *et al.* 1981; (20) Sorochenko, Tolmachev, and Winnewisser 1984; (21) Guelin, Friberg, and Mezaoui 1982.

The data on C<sup>18</sup>O emission and H<sub>2</sub>CO absorption predominantly come from maps of several dark clouds. For C<sup>18</sup>O, maps of 3C 111 (Ungerer *et al.* 1985), L1495 (Duvert, Cernicharo, and Baudry 1986), and HCL2 (Cernicharo and Guelin 1987) are used. Maps of H<sub>2</sub>CO absorption at 6 cm for TMC-2 (Pöppel, Rohlfs, and Celnik 1983), globules near NGC 2264 (Minn and Greenberg 1979), HCL2 (Sherwood and Wilson 1981) and L1709 (Minn and Greenberg 1987) are incorporated into the compilation. In addition to these maps, individual positions, usually the cloud core, have been observed; measurements of C<sup>18</sup>O by Baudry *et al.* (1981) and Myers, Linke, and Benson (1983) and of H<sub>2</sub>CO by Cohen *et al.* (1983) are included.

For ammonia and the complex molecules, measurements of cloud cores represent the majority of the data compiled. The cores used in the compilation and the molecular results appear in Table 2. The (0, 0) positions for most cores are from Myers, Linke, and Benson (1983). The core positions for TMC-3A and L183S are from Churchwell, Nash, and Walmsley (1984), and the position for HCL2-B is from Cernicharo, Guelin, and Askne (1984). Separate observations within 2' of a given position are considered together in the compilation. If the separate observations are of the same molecule, the resulting column densities are an average for the specific position. Furthermore, maps of TMC-1 (Tölle *et al.* 1981; Guelin, Friberg, and Mezaoui 1982; Gaida, Ungerechts, and Winnewisser 1984) and of TMC-1A and TMC-1C (Cernicharo, Guelin, and Askne 1984) are utilized.

Most of the sources of data have presented results in terms of column densities. The sources listed in Table 1 have derived the C<sup>18</sup>O column density in essence under the assumption of LTE. Myers, Linke, and Benson (1983) and Ungerer *et al.* (1985) have improved upon this assumption somewhat by specifically estimating the optical depth and excitation temperature, but as pointed out by Myers, Linke, and Benson, the results are comparable to those of LTE. The formaldehyde data have been made self-consistent by always using an excitation temperature of 1.7 K to obtain  $N(\text{H}_2\text{CO})$  of the  $1_{11}$  state (Cohen *et al.* 1983); slightly different values for the excitation temperature would displace the data in the figure by less than 0.1 dex. The column density (in units of  $\text{cm}^{-2}$ ) in the  $1_{11}$  state has been derived from

$$N(\text{H}_2\text{CO}) = 2.3 \times 10^{13} W, \quad (4)$$

where the equivalent width  $W$  equals  $T_L$  times  $\Delta v$  (Minn and Greenberg 1979, 1987). The line temperature is  $T_L$ , and  $\Delta v$  is the full width at half-intensity of the line. Pöppel, Rohlfs, and Celnik (1983) have tabulated their results in terms of equivalent widths; equation (4) has been used to derive the corresponding column densities.

The column densities for NH<sub>3</sub>, HC<sub>3</sub>N, HC<sub>5</sub>N, and C<sub>4</sub>H are based on statistical equilibrium, usually large velocity gradient, models. Gaida, Ungerechts, and Winnewisser (1984), however, obtained the optical depth and excitation for NH<sub>3</sub> emission from profile fitting. For several cloud cores, multiple measurements for NH<sub>3</sub> and HC<sub>3</sub>N exist, and the derived column densities spanned a range of at most, and usually less than, a factor of 3. This fact gives us confidence in the values for column density used in our analysis. For C<sub>4</sub>H, data of Guelin, Friberg, and Mezaoui (1982) are somewhat arbitrarily scaled to the data of Cernicharo, Guelin, and Askne (1984) because (1) the two data sets revealed similar slopes in plots of  $N(\text{C}_4\text{H})$  versus either  $N(\text{HC}_5\text{N})$  or  $N(\text{HC}_3\text{N})$  but were offset

TABLE 2  
DATA FOR CLOUD CORES

CLOUD	CENTRAL POSITION		OFFSETS <sup>a</sup> ( $\Delta\alpha$ , $\Delta\delta$ )	log $N(X)$				REFERENCES <sup>b</sup>
	$\alpha(1950)$	$\delta(1950)$		$N(\text{NH}_3)$	$N(\text{HC}_3\text{N})$	$N(\text{HC}_5\text{N})$	$N(\text{C}_4\text{H})$	
L1489 .....	04 <sup>h</sup> 01 <sup>m</sup> 45 <sup>s</sup> 0	26°10'33"	(0, 0)	15.22	...	12.40	...	1, 2
L1498 .....	04 07 50.0	25 02 13	(0, 0)	14.90	...	12.80	...	1
L1495 .....	04 10 57.5	28 03 13	(0, 0)	14.90	...	12.20	...	1
L1521B .....	04 21 08.5	26 30 00	(0, 0)	...	13.15	13.20	...	1, 3
L1400K .....	04 26 51.0	54 45 27	(0, 0)	14.60	...	12.10	...	1
TMC-2A .....	04 28 58.4	24 24 27	(0, 0)	15.50	12.82	...	...	2, 4
TMC-2 .....	04 29 43.0	24 18 54	(0, 0)	14.88	13.41	13.00	13.93	1, 2, 3, 4, 5, 6
L1536B .....	04 30 21.7	22 38 10	(0, 0)	14.80	12.63	12.50	...	1, 3
TMC-3A .....	04 32 32.2	24 02 40	(0, 0)	14.75	12.77	...	...	5
HCL2-B .....	04 36 47.0	25 58 15	(0, 0)	14.70	13.10	12.60	14.00	7
TMC-1A .....	04 36 55.0	25 36 55	(0, 0)	14.90	13.00	12.60	14.30	7
			(0, 5)	14.20	13.20	12.60	14.20	7
			(0, 7.5)	14.20	13.30	12.60	14.30	7
TMC-1C .....	04 38 32.0	25 55 00	(0, 0)	14.91	13.87	13.05	14.60	1, 5, 7
			(2.5, -2.5)	14.80	13.00	...	...	7
			(1.25, -2.5)	14.60	...	12.20	14.00	7
			(2.5, -1.25)	14.90	13.00	...	...	7
			(1.25, -1.25)	15.10	13.60	13.00	14.50	7
			(0, -1.25)	14.90	13.40	12.60	14.30	7
			(2.5, 0)	14.90	13.20	...	...	7
			(1.25, 0)	15.00	13.40	12.90	14.20	7
			(-1.25, 0)	14.80	13.40	12.80	14.10	7
			(-2.5, 0)	14.90	13.20	12.30	...	7
			(0, 1.25)	14.90	13.30	12.60	14.20	7
			(-1.25, 1.25)	14.90	13.20	12.50	...	7
			(-2.5, 1.25)	14.80	13.50	12.80	...	7
			(-2.5, 2.5)	...	...	12.60	...	7
			(-1.25, 2.5)	14.40	...	...	...	7
			(0, 2.5)	14.60	...	...	...	7
TMC-1 .....	04 38 42.0	25 35 45	(0, 0)	...	13.69	13.60	14.53	1, 2, 3, 6, 8
			(-4, 6)	15.10	...	...	13.92	2, 6
			(-2, 4)	14.91	...	...	14.15	2, 6
			(3.5, -4)	...	...	...	14.26	2, 6
			(1.67, 2.5)	...	13.60	13.40	...	8
			(0.83, 1.25)	...	13.60	13.40	...	8
			(-0.83, -1.25)	...	13.80	13.40	...	8
			(-1.67, -2.5)	...	13.70	13.40	...	8
L1517B .....	04 52 02.6	30 32 18	(0, 0)	14.80	...	12.40	...	1, 2
L1512 .....	05 00 54.5	32 40 00	(0, 0)	14.90	...	12.90	...	1
L1544 .....	05 01 14.0	25 07 00	(0, 0)	15.33	13.45	13.40	13.81	1, 2, 3, 5, 6
L134 .....	15 50 53.0	-04 28 13	(0, 0)	...	...	...	14.39	6
L183S .....	15 51 32.7	-02 42 51	(0, 0)	...	12.60	...	13.32	4, 5, 6
L183 .....	15 51 35.7	-02 40 54	(0, 0)	15.35	12.91	12.30	...	1, 3, 5
L43E .....	16 31 48.5	-15 40 33	(0, 0)	14.80	...	12.40	...	1
L63 .....	16 47 21.0	-18 01 00	(0, 0)	15.00	12.57	12.10	13.49	1, 4, 6
L778 .....	19 24 26.4	23 52 37	(0, 0)	14.80	...	12.30	...	1
L1172A .....	21 01 48.6	67 42 13	(0, 0)	15.00	...	12.90	...	1
L1031B .....	21 45 32.0	47 18 12	(0, 0)	...	...	12.50	...	1

<sup>a</sup> Offsets are in arcminutes.

REFERENCES.—(1) Benson and Myers 1983; (2) Gaida, Ungerechts, and Winnewisser 1984; (3) Sorochenko, Tolmachev, and Winnewisser 1984; (4) Bujarrabal *et al.* 1981; (5) Churchwell, Nash, and Walmsley 1984; (6) Guélin, Friburg, and Mezaoui 1982; (7) Cernicharo, Guélin, and Askne 1984; (8) Tölle *et al.* 1981.

from each other by 0.2–0.4 dex and (2) different transitions were analyzed. Since we are mainly interested in the slopes of relationships, the actual scale for  $N(\text{C}_4\text{H})$  is of minor importance.

The values for  $N(\text{H}_2)$  are derived from  $A_V$  using the relationship:  $N(\text{H}_2) = 0.94 \times 10^{21} A_V \text{ cm}^{-2}$  (e.g., Myers, Linke, and Benson 1983). For many of the clouds, especially those in Taurus, the values for  $A_V$  are from Cernicharo and Bachiller (1984). Many of the sources for the molecular data tabulated  $A_V$  as well. The derivation of  $A_V$  involves uncertainties at the 15%–20% level, and when  $A_V \geq 6$  mag, such a value is regarded as a lower limit (see, e.g., Cernicharo and Bachiller 1984).

We limit ourselves to positions with  $A_V \geq 1$  mag, where most of the gas is expected to be  $\text{H}_2$ , thereby allowing us to apply the above expression between  $N(\text{H}_2)$  and  $A_V$ .

### III. RELATIONSHIPS FOR OXYGEN-BEARING SPECIES

#### a) CO

The ultraviolet measurements of CO and  $\text{H}_2$  in diffuse clouds reveal that  $N(\text{CO})$  varies quadratically with  $N(\text{H}_2)$  (Federman *et al.* 1980). Federman and Lambert (1988) showed that this trend continued in moderately reddened directions by plotting  $N(\text{CO})$  versus  $N(\text{CH})$ ;  $N(\text{CH})$  was used because this

molecule increases linearly with  $N(\text{H}_2)$  for directions with  $A_V \leq 4$  mag (Cardelli and Wallerstein 1986; Mattila 1986). Since the effects of self-shielding of the CO lines responsible for CO photodissociation occur at  $N(\text{CO}) \geq 10^{16} \text{ cm}^{-2}$  (Glassgold, Huggins, and Langer 1985; van Dishoeck and Black 1988), the results for dark clouds are important for the CO chemistry. Results from the Bordeaux telescope (see Table 1) indicate that for dark clouds,  $N(\text{C}^{18}\text{O})$  is directly proportional to  $A_V$  or equivalently  $N(\text{H}_2)$ . There is considerable scatter in the data points for some of the clouds, however, and a nonlinear relationship may be more appropriate. We have investigated this possibility by compiling the data in a log-log plot so that we may derive the slope applicable to the kinetics of CO.

Figure 1 shows the results of the compilation for CO. Maps of entire dark clouds and selected observations of dark cloud cores in the  $J = 1 \rightarrow 0$  line of  $\text{C}^{18}\text{O}$  are used in the analysis (see Table 1). The  $\text{C}^{18}\text{O}$  data are multiplied by 500, the isotopic ratio applicable to interstellar clouds (Wannier 1980), to obtain  $N(\text{CO})$  from  $N(\text{C}^{18}\text{O})$ . Selective photodestruction of  $\text{C}^{18}\text{O}$  relative to CO may require the use of a slightly larger isotopic ratio (Bally and Langer 1982); the recent analysis of the photodestruction of carbon monoxide by van Dishoeck and Black (1988) indicates that the appropriate ratio may be closer to 1500. Increasing the ratio by  $\sim 3$  would affect the display in Figure 1a slightly. The polygon representing the dark cloud would have to be raised 0.5 dex.

The presentation in Figure 1b, which concentrates on the dark cloud data, is discussed first. The data for several clouds, including cloud cores, show a strong correlation with a slope of  $\sim 1.5$ . For several hundred data points, a correlation coefficient  $r$  of 0.78 is highly significant. However, the data for  $N(\text{H}_2)$  in the cloud cores are probably lower limits because of the large extinctions associated with the cores— $A_V \geq 5-6$  mag. If greater values for  $N(\text{H}_2)$  were more appropriate for these data, the data should be moved an unknown amount to the right, suggesting a flatter relationship for  $\log [N(\text{H}_2)] > 21.75$ . A constant abundance is inferred from a slope of unity in plots

similar to Figure 1b. (In such plots, abundances can be derived because in cloud envelopes the two species occupy similar volumes.) A slope greater than unity indicates that the abundance of CO continues to increase for clouds with  $N(\text{H}_2)$  between  $1 \times 10^{21} \text{ cm}^{-2}$  and  $5-6 \times 10^{21} \text{ cm}^{-2}$ . This result contradicts the conclusions of Ungerer *et al.* (1985), Duvert, Cernicharo, and Baudry (1986), and Cernicharo and Guelin (1987); based on linear plots, these studies found no change in the abundance of  $\text{C}^{18}\text{O}$ . An appreciable amount of dispersion, which could mask a relationship with a slope somewhat greater than 1, is seen in their linear plots. Any flattening of the relationship beyond  $N(\text{H}_2) \sim 5 \times 10^{21} \text{ cm}^{-2}$  would suggest that  $\text{C}^{18}\text{O}$  samples only the outer regions of a dark cloud, contrary to commonly held belief.

A comparison between CO and  $\text{H}_2$  measurements of diffuse clouds and the measurements of  $\text{C}^{18}\text{O}$  and  $A_V$  for dark clouds is illustrated in Figure 1a. As noted previously by Federman *et al.* (1980), the diffuse cloud data show a definite trend, and Figure 1a indicates that this trend is nearly continuous when the dark cloud data are included. This result bears on the models of the self-shielding of CO to photodissociation. In the case for  $\text{H}_2$ , the ultraviolet data indicate a sharp (factor of  $10^4$ ) transition as the lines become optically thick to dissociating radiation (Savage *et al.* 1977). No sharp transition is apparent in our compilation for CO. Linear least-squares fits to the diffuse cloud data and the dark cloud data indicate a factor of 6 jump in  $N(\text{CO})$  at  $N(\text{H}_2)$  of  $10^{21} \text{ cm}^{-2}$ . An increase in the isotopic ratio between  $\text{C}^{18}\text{O}$  and CO only changes this conclusion slightly. The analysis of CO self-shielding by van Dishoeck and Black (1988) reveals that the sharpness of the transition depends on the incident flux of dissociating radiation. Their results suggest that a radiation field about half of the flux deduced for the local Galactic environment can reproduce the variation seen in Figure 1. A slight reduction caused by attenuation of the average Galactic radiation field in the diffuse envelope ( $A_V \leq 1$  mag) of a cloud seems appropriate.

Several points regarding the compilation of CO data require additional comment. Foremost, calculations for selective

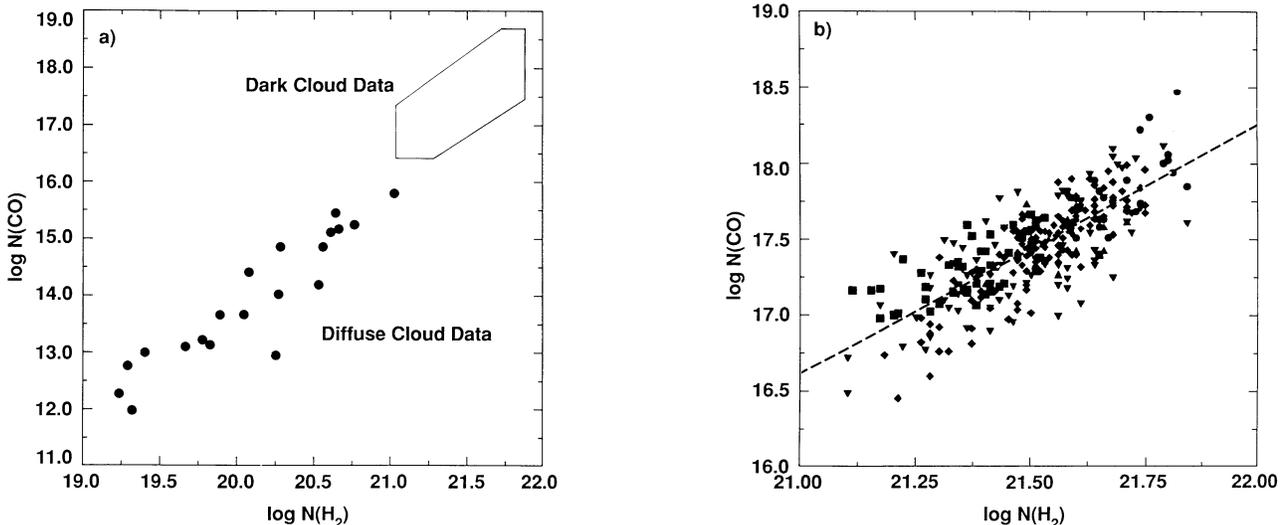


FIG. 1.—A plot of  $\log N(\text{CO})$  vs.  $\log N(\text{H}_2)$ . (a) Comparison of diffuse cloud data with dark cloud data. (b) Expanded view of dark cloud with the following sources: cores (circles) from Myers, Linke, and Benson (1983) and (triangles) from Baudry *et al.* (1981); (squares) for 3C 111—Ungerer *et al.* (1985); (inverted triangles) for L1495—Duvert, Cernicharo, and Baudry (1986); (diamonds) for HCL2—Cernicharo and Guelin (1987). Dashed line indicates a linear fit to the data with a slope of 1.6.

photodissociation do not yet yield a quantitative value for the conversion factor from  $C^{18}O$  to CO. The laboratory measurements on CO of Letzelter *et al.* (1987) were acquired at room temperature; thus, an unknown fraction of the predissociation seen by them may arise in absorption from rotational levels not populated at interstellar temperatures. van Dishoeck and Black (1988) acknowledge this uncertainty in their calculation of selective photodissociation and estimate the range of applicability to be a factor of 2. If at interstellar temperatures fewer transitions lead to photodissociation, an isotopic ratio approaching the terrestrial value of 500, the value used by us, would be appropriate. Second, should the isotopic ratio be larger than the terrestrial value, Figure 11 of van Dishoeck and Black (1988) indicates an increasing value in  $C^{18}O/CO$  for  $A_V$  between 2 and 4 mag. The factor of 2 increase in the ratio  $C^{18}O/CO$ , comparable to the largest uncertainties expected in the analysis, would raise the data with values of  $\log [N(H_2)] \sim 21.30$  preferentially. The result would be a slope approaching 2 for smaller values of  $N(H_2)$  and a slope somewhat less than 1.5 at larger values of  $N(H_2)$ . Third, the theoretical curves of van Dishoeck and Black reveal a nonlinear relationship between  $N(CO)$  and  $N(H_2)$ , a result that conflicts with the linear correlations found by Ungerer *et al.* (1985), Duvert, Cernicharo, and Baudry (1986), and Cernicharo and Guelin (1987). Our log-log presentation indicates a slope of  $\sim 1.5$ , a value more in line with the theoretical results. Last, a slope of  $\sim 1.5$  indicates that the abundance of CO continues to increase for molecular material with  $A_V$  of 1–4 mag. The increase in CO abundance occurs in the same portions of a cloud that optical observations show a decrease in  $C^+$  abundance (e.g., Federman and Huntress 1989). The carbon ion is being chemically processed into the stable CO molecule.

We have not included the results of Frerking, Langer, and Wilson (1982) because of the potential problem with their comparisons between  $N(C^{18}O)$  and  $A_V$  (see Cernicharo and Guelin 1987). van Dishoeck and Black (1988) suggested that the two sets of observations can be reconciled by allowing somewhat larger uncertainties in the measured parameters. In any case, the addition of the small number of data from Frerking, Langer, and Wilson would not alter our findings.

More important to our analysis are some of the conclusions of Frerking, Langer, and Wilson (1982). Their results show (1) direct evidence for self-shielding through a break in the relationships between  $N(C^{18}O)$  or  $N(^{13}CO)$  and  $A_V$  [or  $N(H_2)$ ] at a column density of  $\sim 10^{14} \text{ cm}^{-2}$  and (2) a nonlinear relationship with  $A_V$  because of the break. The break is an indication of where self-shielding is playing a role. A break in the relationship for  $N(C^{18}O)$  at  $\sim 10^{14} \text{ cm}^{-2}$  corresponds to a break in the relationship for  $N(CO)$  at  $\sim 10^{16} \text{ cm}^{-2}$ , as found here. However, their conclusions and those of Bally and Langer (1982) refer to breaks for all isotopic variants at  $\sim 10^{14} \text{ cm}^{-2}$ . We do not see a break in our compilation until  $N(CO)$  reaches a value of  $\sim 10^{16} - 10^{17} \text{ cm}^{-2}$ , consistent with the results of van Dishoeck and Black (1988). The relatively tight correspondence between  $N(CO)$  and  $N(H_2)$  for column densities less than  $10^{16} \text{ cm}^{-2}$  merits a closer theoretical examination of the self-shielding process. Frerking, Langer, and Wilson also found indications of saturation in the  $C^{18}O$  lines above extinctions of  $\sim 6$  mag, a result implying that the relationship between  $N(CO)$  and  $N(H_2)$  remains nonlinear beyond  $\log [N(H_2)] \sim 21.75$ . A nonlinear relationship cannot continue much beyond this column density in  $H_2$ , however, because the abundance of CO is not likely to exceed a value of  $\sim 10^{-4}$ .

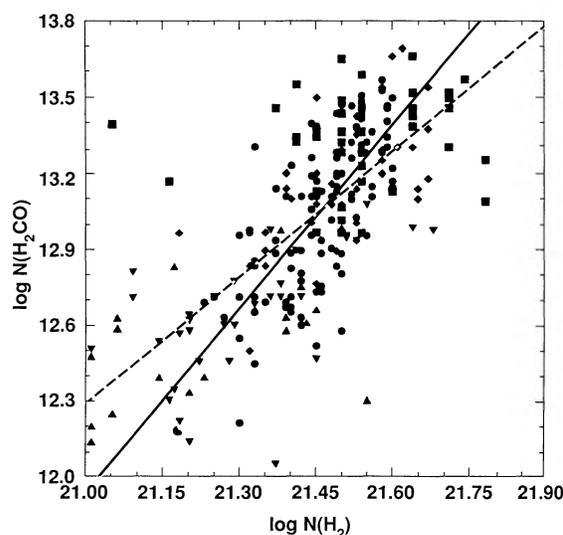


FIG. 2.—Compilation of 6 cm  $H_2CO$  data plotted against  $N(H_2)$ . The sources for the data are (circles) Pöppel, Rohlfs, and Celnik (1983)—TMC-2; (squares) Minn and Greenberg (1979)—globules near NGC 2264; (diamonds) Sherwood and Wilson (1981)—HCL2; (triangles) Cohen *et al.* (1983)—various sources; (inverted triangles) Minn and Greenberg (1987)—L1709. Two linear fits are shown: the thin line with a slope of 2.33 based on the data of Pöppel, Rohlfs, and Celnik and the dashed line with a slope of 1.62 based on all the data.

#### b) $H_2CO$

Our compilation of 6 cm  $H_2CO$  observations is presented in Figure 2; the references appear in Table 1. Data for the  $\rho$  Oph Cloud (e.g., Myers *et al.* 1978) and for the  $\epsilon$  Cha I dark cloud (Toriseva and Mattila 1985) are not included because these data sample regions where significant amounts of star formation are taking place. Such data fall below the data shown in Figure 2 by  $\sim 0.3$  dex, even for  $A_V$  approaching 4 mag, indicating that enhanced ultraviolet flux from the nearby star formation readily dissociates  $H_2CO$ . We have placed the highest weight on the data of Pöppel, Rohlfs, and Celnik (1983) because of the number of data points in their study of TMC-2 (L1529) and because they used the 100 m telescope at Bonn which has the highest spatial resolution available at 6 cm.

The data of Pöppel, Rohlfs, and Celnik (1983) show a correlation with  $N(H_2)$ . The slope of the relationship is 2.33; the correlation is quite strong with  $r$  equaling 0.70 for 107 data points. The combined set of data reveals a slightly smaller slope of 1.62, but a similar degree of correlation ( $r = 0.69$  for over 200 data points). A synthesis of these two results suggests that  $N(H_2CO)$  varies approximately in a quadratic manner with  $N(H_2)$ . Different relationships are found from individual  $H_2CO$  studies when the data are displayed on linear axes. For example, no correlation was seen by Minn and Greenberg (1979) for globules near NGC 2264, but a correlation indicating direct proportionality appeared in the data of Sherwood and Wilson (1981) for HCL-2. As discussed in the introduction, difficulties arise with such analyses. The compiled set of data, therefore, are graphed in a log-log fashion.

Photodissociation of  $H_2CO$  is likely to be important for visual extinctions approaching 4 mag because  $H_2CO$ , which has two relatively weak hydrogen bonds, is readily destroyed by photons with wavelengths greater than 1200–1300 Å (Suto, Wang, and Lee 1986). This fact translates into a thicker region of photodissociation for  $H_2CO$  compared to the region appropriate for the more tightly bound molecules  $C_2$  and CN, which are dissociated by photons with  $\lambda \leq 1200 - 1300 \text{ Å}$  (Pouilly *et*

*al.* 1983 for C<sub>2</sub>; Lavendy, Robbe, and Gandara 1987 for CN). Since H<sub>2</sub>CO is destroyed by redder photons than are C<sub>2</sub> or CN, and since the amount of extinction increases with a decrease in wavelength (see Code *et al.* 1976), the photochemical regime of H<sub>2</sub>CO penetrates deeper into a cloud. Moreover, the fact that gas phase reactions are less efficient at destroying H<sub>2</sub>CO enhances the importance of photodissociation. For example, the reaction involving H<sub>2</sub>CO and O occurs at a relatively slow rate (e.g., Washeda, Martinez, and Bayes 1974). (Ion-molecule reactions tend to recycle formaldehyde.)

For the highest values of  $N(\text{H}_2)$ , which as mentioned above for CO are probably lower limits, the slope between  $\log N(\text{H}_2\text{CO})$  and  $\log N(\text{H}_2)$  may actually decrease because the relationship levels off. The likelihood of sampling the portion of cloud where H<sub>2</sub>CO is photodissociated and the possibility of a decreasing slope indicate that 6 cm measurements of H<sub>2</sub>CO always arise from the outer regions of dark clouds. This conclusion was reached previously by Vanden Bout, Snell, and Wilson (1983), who partially mapped several dark clouds in the 6 cm transition. Minn and Greenberg (1987) suggested that depletion onto grains is the cause of the decrease in slope as observations probe the core of the cloud.

Finally, we want to stress that the observational data presented in Figure 2 are in disagreement with pure gas-phase photochemical equilibrium models. The theoretical estimates are significantly lower than the observed column densities. We hope that this compilation will be useful in improving our theoretical understanding.

#### IV. RELATIONSHIPS FOR NITROGEN-BEARING MOLECULES

##### a) NH<sub>3</sub>

Ammonia is one of the simplest nitrogen-bearing species predicted to be abundant in dark clouds; readily detectable lines at radio wavelengths make NH<sub>3</sub> a species commonly observed in molecular clouds. The excitation conditions for emission of NH<sub>3</sub> (densities  $\sim 10^4 \text{ cm}^{-3}$ ) occur in the core regions of dark clouds (Benson and Myers 1983). Thus  $N(\text{NH}_3)$  is not expected to correlate with  $A_\nu$  or  $N(\text{H}_2)$ , which sample both high- and low-density regions within a cloud. This fact is borne out in our compilation. A more appropriate molecule to compare with NH<sub>3</sub> may be C<sup>18</sup>O, which because of its low isotopic abundance, samples deeper into the cloud than does CO. Figure 3 shows the correspondence between  $N(\text{NH}_3)$  and  $N(\text{C}^{18}\text{O})$ . A somewhat surprising result first noted by Benson and Myers (1983) is that there is no correlation between these two molecules. One possible reason for the lack of a correlation may be that the NH<sub>3</sub> only resides in clumps within the core.

Millar and Freeman (1984*a, b*) offered the suggestion that reactions involving atomic nitrogen lead to the cyanopolyynes. If atomic nitrogen is also involved in the production of NH<sub>3</sub>, as was thought to be the case in earlier models (Millar and Freeman 1984*a*), then we expect some correlation between ammonia and the cyanopolyynes. We investigate this by plotting  $\log N(\text{HC}_3\text{N})$  and  $\log N(\text{HC}_5\text{N})$  against  $\log N(\text{NH}_3)$  in Figures 4 and 5. No correlation is seen in either plot, implying that reactions such as



are not important in the production of NH<sub>3</sub>. We interpret this result as an astronomical substantiation of previous analyses

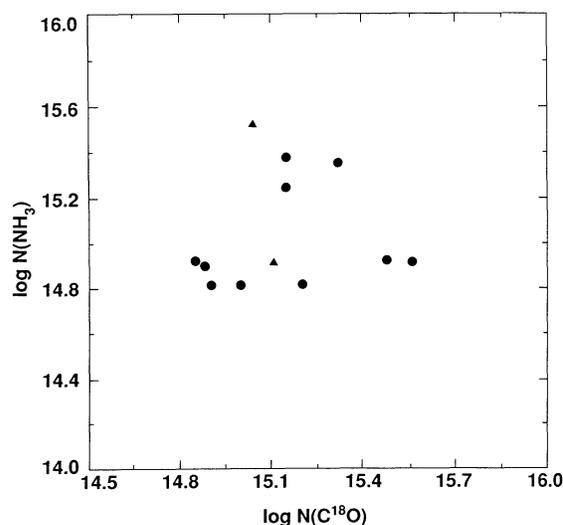
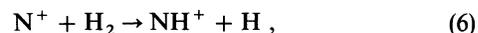


FIG. 3.—Comparison of  $\log N(\text{NH}_3)$  and  $\log N(\text{C}^{18}\text{O})$ . The sources are (circles) Benson and Myers (1983) in combination with the other references listed in Table 1 for cores and (triangles) Cernicharo, Guelin, and Askne (1984) and Gaida, Ungerechts, and Winnewisser (1984) for clouds in Taurus.

of the reaction dynamics of equation (5) (Huntress 1977; Herbst, Defrees, and McLean 1987). When the fine structure of  $\text{N}^+$  is taken into account (Galloway and Herbst 1989), or when the kinetic energy of  $\text{N}^+$  from the dissociative charge transfer of  $\text{He}^+$  on  $\text{N}_2$  is considered (Yee, Lepp, and Dalgarno 1987), the reaction



is sufficiently rapid nearly to produce the observed amount of NH<sub>3</sub> (Herbst and Leung 1989). Langer and Graedel (1989) also found that the abundance of NH<sub>3</sub> relative to H<sub>2</sub> in TMC-1 can be reproduced by incorporating reactions between  $\text{CH}_3^+$  and N.

An important fact is revealed in Figures 3–5, especially the

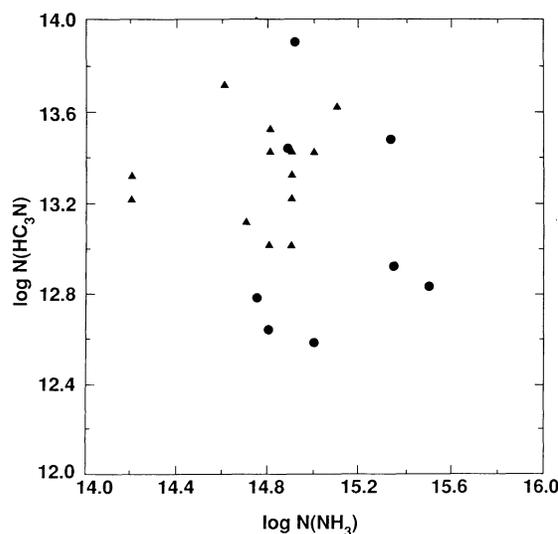


FIG. 4.—Same as Fig. 3 for HC<sub>3</sub>N and NH<sub>3</sub>. (triangles): from Cernicharo, Guelin, and Askne (1984) for Taurus sources. (circles): from a combination of Bujarrabal *et al.* (1981), Benson and Myers (1983), Churchwell, Nash, and Walmsley (1984), Gaida, Ungerechts, and Winnewisser (1984), and Sorochenko, Tolmachev, and Winnewisser (1984).

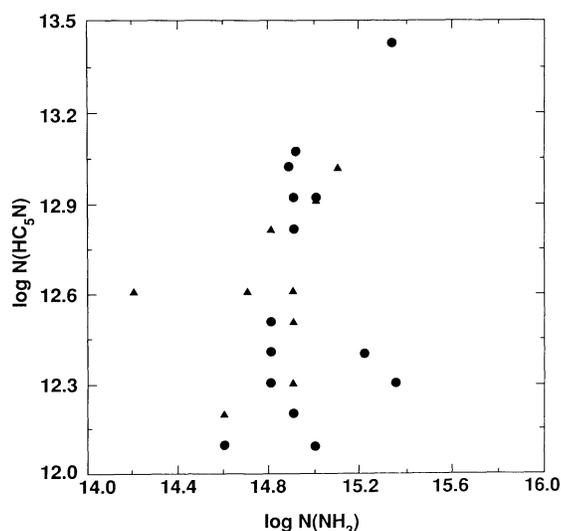


FIG. 5.—Same as Fig. 3 for  $\text{HC}_5\text{N}$  and  $\text{NH}_3$ . Symbols represent the same data sources as in Fig. 4.

latter two:  $\log N(\text{NH}_3)$  is always 15! While the other molecules studied here show systematic variations in column density of factors of 10–100, the column density of  $\text{NH}_3$  is constant to within a factor of 3. The constancy in  $N(\text{NH}_3)$  may be due to unusual chemical processes or excitation conditions for  $\text{NH}_3$ . At the present time, however, we place more emphasis on a better understanding of the excitation conditions.

Maps of ammonia and cyanopolyne emission from TMC-1 reveal distinctly different distributions (Tölle *et al.* 1981; Olano, Walmsley, and Wilson 1988). The general conclusion has been that real abundance variations are present, although Bujarrabal *et al.* (1981) interpreted the differences in terms of differences in excitation. Our finding that  $N(\text{NH}_3) \sim 10^{15} \text{ cm}^{-2}$ , with little dispersion about this value for an ensemble of clouds, may hold the clue to resolving this issue.

#### b) Complex Molecules: $\text{HC}_3\text{N}$ , $\text{HC}_5\text{N}$ , and $\text{C}_4\text{H}$

Most comparisons between complex molecules have been restricted to two dark clouds, TMC-1 and L183 (L134N). Here we incorporate appropriate data for as many clouds as possible, especially the surveys of dark cloud cores of Myers and collaborators. The comparison of  $N(\text{HC}_5\text{N})$  with  $N(\text{HC}_3\text{N})$  is shown in Figure 6. For this compilation, two points are worthy of mention. First, a strong correlation with a slope of 1 and a correlation coefficient of 0.78 exists between these molecules for all the cores. This result indicates that, as expected, the chemistries of these two molecules are connected. Second, the data show that for all dark cloud cores, not just TMC-1,  $N(\text{HC}_3\text{N}) \sim 3 N(\text{HC}_5\text{N})$ , a result noted previously by Bujarrabal *et al.* (1981) and Snell *et al.* (1981) for a smaller sample. Such a “universal” ratio places constraints on the mechanisms for building the carbon chains.

As can be discerned from Figure 7, a possible correlation exists between  $\text{HC}_5\text{N}$  and  $\text{C}^{18}\text{O}$ . The correlation coefficient is small, however ( $r \sim 0.40$ ). Benson and Myers (1983) obtained a similar result for these data and attributed it to two distinct populations of clouds: those in Taurus and those elsewhere. We believe that the weakness of the correlation most likely arises because the two molecules are not chemically related, nor are they spatially coexistent. Since the data for  $\text{HC}_5\text{N}$  sampled the dense, core region, the weak correlation indicates

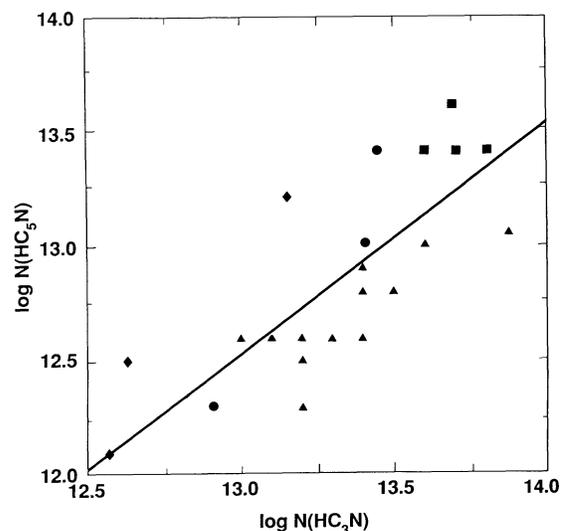


FIG. 6.—Same as Fig. 3 for  $\text{HC}_5\text{N}$  and  $\text{HC}_3\text{N}$ . The following sources of data were used: (circles) Benson and Myers (1983) in combination with Churchwell, Nash, and Walmsley (1984); (triangles) Cernicharo, Guelin, and Askne (1984); (squares) Tölle *et al.* (1981); (diamonds) Benson and Myers in combination with Gaida, Ungerechts, and Winnewisser (1984). The thin line indicates a least-squares linear fit to the data with a slope of 1.

that the observed  $\text{C}^{18}\text{O}$  may *not* reside in the core. This result is consistent with a decrease in slope at large  $N(\text{H}_2)$  in Figure 1b.

The processes for producing the long-chain molecule  $\text{C}_4\text{H}$  are expected to be similar to those for the cyanopolyynes. The results of our compilation for  $N(\text{C}_4\text{H})$  are plotted against  $N(\text{HC}_5\text{N})$  in Figure 8; a similar correspondence is found between  $\text{C}_4\text{H}$  and  $\text{HC}_3\text{N}$ . Again, a correlation is present; the slope is approximately 0.5, and  $r$  is about 0.80. The correlation was first noted by Millar and Freeman (1984a). The correspondence between carbon-chain molecules both with and without nitrogen leads to the suggestion that all long-chain molecules are formed through similar processes; for example, reactions involving acetylene can build the backbone of these molecules

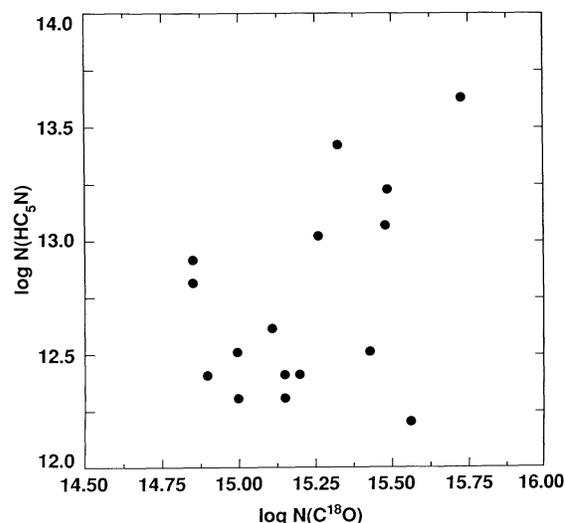


FIG. 7.—Same as Fig. 3 for  $\text{HC}_5\text{N}$  and  $\text{C}^{18}\text{O}$ , where the data are from Myers and collaborators.

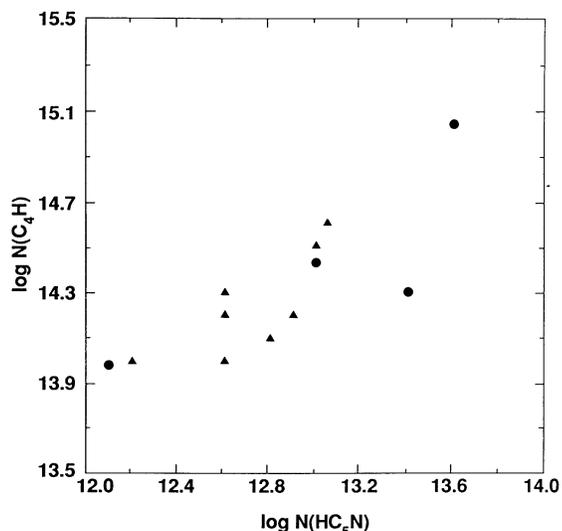


FIG. 8.—Same as Fig. 3 for  $C_4H$  and  $HC_5N$ . The data of Guelin, Friberg, and Mezaoui (1982) (circles) have been scaled to the data of Cernicharo, Guelin, and Askne (1984) (triangles).

(Mitchell and Huntress 1979; Schiff and Bohme 1979). More data are needed to substantiate this finding.

The results of Snell *et al.* (1981) have not been included in our compilation, primarily for two reasons. Their data for L134N (L183) were acquired at a different position than the data of Myers and collaborators, and their column densities are significantly lower for many of the clouds in common with the more recent work presented above. A large part of the differences in column density probably resides in the fact that Snell *et al.* derived  $N(HC_3N)$  from physical conditions, which were obtained by analyzing  $HC_5N$  emission, assuming optically thin emission from  $HC_3N$ , and applying a large velocity gradient model of radiative transfer to the data. The correspondence between  $HC_5N$  and  $HC_3N$  that we found in Figure 6 probably arises from chemical ties and need not indicate spatial coexistence. Other observational results, based in part on analyzing the emission of hyperfine components, found moderate optical depths for  $HC_3N$  emission (e.g., Cernicharo, Guelin, and Askne 1984; Sorochenko, Tolmachev, and Winnewisser 1986). Thus, Snell *et al.* may have underestimated  $N(HC_3N)$  through an incorrect assessment of density and through a neglect of line saturation.

#### V. SUMMARY

We analyzed the chemistry of dark clouds from an empirical perspective. Correlations among measured column densities were sought. The slopes arising from log-log plots were determined because these slopes provide constraints for the chemistry of interstellar molecules and for the physical structure of the cloud.

We find that when  $C^{18}O$  data are converted to CO through

the use of a constant ratio of 500, the slope in the relationship between CO column density and  $H_2$  column density in clouds with  $A_V \leq 4$  mag is  $\sim 1.5$ . This result indicates that the abundance of CO increases with depth in the outer regions of dark clouds, but less steeply with  $N(H_2)$  than in diffuse clouds with  $A_V \leq 1$  mag. A factor of 6 jump occurs at  $N(H_2)$  of  $10^{21} \text{ cm}^{-2}$  between the column density for CO in dark clouds and that in diffuse clouds, a result that places constraints on the strength of the UV field responsible for the photodissociation of CO. Measurements of the 6 cm line of  $H_2CO$  indicate that  $N(H_2CO)$  increases quadratically with  $N(H_2)$  for  $A_V \leq 4$  mag, but that the relationship probably flattens for data appropriate to  $A_V \geq 4$  mag, where only lower limits for  $N(H_2)$  are available.

The data on nitrogen compounds and carbon-chain molecules discussed in § IV also reveal information.  $N(NH_3)$  is a nearly constant value of  $\sim 10^{15} \text{ cm}^{-2}$  for all clouds sampled. Because of recent progress in the understanding of ammonia chemistry, a cause for the constant column density may arise from excitation. There is a highly significant correlation between  $N(HC_5N)$  and  $N(HC_3N)$  with a slope of unity. This relationship strongly suggests that the chemistry of these two species is connected. Moreover, the data for several dark clouds indicates that the value of  $\sim 3$  for the ratio  $N(HC_3N)/N(HC_5N)$  is universal, i.e., not specific to TMC-1. The weakness of the correlation between the cyanopolyynes and  $C^{18}O$  favors the conclusion that the molecules are spatially distinct. Although the amount of appropriate data is sparse, the cyanopolyynes also appear correlated with  $C_4H$ , from which we infer a common origin for carbon-chain molecules with acetylene playing a crucial role.

We have not discussed several other important molecules that are relatively easily observed; these include CH, OH, and  $C_2H$ . Mattila (1986) analyzed in detail the 9 cm observations of CH in dark clouds. More ultraviolet data from diffuse clouds and more 18 cm data from dark clouds taken at high spatial resolution are needed to study OH. Wootten *et al.* (1980) partially mapped several dark clouds in lines of  $C_2H$ ; additional data are required before definitive statements regarding trends can be made.

These results add essential ingredients to models of the chemical and physical conditions in interstellar clouds. Knowledge of how strongly the column density of one molecule correlates with that for another molecule and knowledge of the slope and the intercept in the logarithmic relation provide clues to the underlying chemistry for the molecules and to the physical model for the cloud.

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S. R. FEDERMAN: Department of Physics and Astronomy, The University of Toledo, Toledo, OH 43606

W. T. HUNTRESS, JR.: Earth Science and Applications Division, NASA Headquarters, Washington, DC 20546

S. S. PRASAD: Space Science Center (SHS-274), University of Southern California, University Park, MC-1341, Los Angeles, CA 90089-1341