TOTAL-TO-SELECTIVE EXTINCTION AND THE FORMATION OF MOLECULES IN DIFFUSE INTERSTELLAR CLOUDS

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ABSTRACT

Recent work of Cardelli, Clayton, and Mathis has shown that there is a strong correlation between total-to-selective extinction, R, and the level of UV extinction relative to the visual, A_v. In particular, $\langle A_{uv}/A_v \rangle$ decreases as R increases. In this paper, I examine the dependency of the abundances of CH and H_2 on R for a sample of diffuse clouds with $A_v < 2$ mag. By dividing the sample into two R subgroups, I find that $\langle N(CH) \rangle$ and $\langle N(H_2) \rangle$ decrease by about factors of 4 and 3, respectively, in going from $\langle R \rangle \approx 2.9$ to 3.9. For H_2, this decrease appears to be consistent with a combination of both the loss of available grain surface area through coagulation and a increase in the UV radiation field through a decrease in A_{uv}. In addition, log $N(CH)/N(H_2)$ exhibits a decrease of ~ 0.18 dex for $\langle R \rangle \approx 3.9$ relative to $\langle R \rangle \approx 2.9$. Using the chemistry of Federman and Lambert, I find that this decrease is consistent with additional photodissociation of CH for the $\langle R \rangle \approx 3.9$ subgroup. Finally, data for lines of sight with $A_v > 2$ mag indicate that the general decrease of $N(CH)$, and probably $N(H_2)$, with R persists for regions where gas-phase chemistry should dominate. This may be consistent with a reduction in the formation rate of H_2 due to the loss of grain surface area through coagulation. Because it can be used to estimate UV extinction, I conclude that R may be a suitable parameter for chemical modeling of diffuse cloud environments.

Subject headings: interstellar: matter — interstellar: molecules

I. INTRODUCTION

The analysis of absorption-line data from interstellar clouds has yielded much information on the physical processes of interstellar gas. Of particular interest are lines of sight for which conditions become suitable for the formation of simple carbon-based diatomic molecules such as CH, CH^+, CN, C_2, and CO. Such lines of sight are important because they supply information pertaining to both the nature of interstellar molecular chemistry and the potential evolution of interstellar clouds (Black 1985, 1986).

Improvements in detectors in recent years have led to a renewal interest in optical molecular line studies and a wealth of new data, particularly for *diffuse* clouds where $E(B-V) \leq 0.5$ mag. Some of these recent studies include; CH: Federman (1982), Danks, Federman, and Lambert (1984); CH^+: Federman (1982), Lambert and Danks (1986); CN: Federman, Danks, and Lambert (1984); C_2: Danks and Lambert 1983, van Dishoeck and de Zeeuw (1984). Comparison with abundances of H_2 (Savage *et al.* 1977; Bohlin, Savage, and Drake 1978) shows that the abundance of CH is linearly dependent on H_2 (Federman 1982; Danks, Federman, and Lambert 1984) for $12 < \log N(CH) \leq 13.5$. Using values of $N(H_2)$ derived from the correlation of H_2 and $E(B-V)$ of Bohlin, Savage, and Drake (1978), Cardelli and Wallerstein (1986) showed that this linearity plausibly extends to $\log N(CH) = 14$. This result has been supported by the work of Mattila (1986) who derived CH abundances from 9 cm emission in a number of dark clouds with $\log N(CH)$ as large as 14.

Some of the data from the above studies have been incorporated into chemical models (Danks, Federman, and Lambert 1984; Federman, Danks, and Lambert 1984; van Dishoeck and Black 1986; Federman and Lambert 1988) for which reasonable comparisons to the observed data have been obtained. Where the effects of photodestruction are important in deter-

mining the equilibrium abundances in diffuse clouds with $A_v < 2$ mag (Black and Dalgarno 1977), among the necessary model input parameters are the effects of dust extinction in the ultraviolet.

Recently, Cardelli, Clayton, and Mathis (1988, hereafter CCM) have shown that total-to-selective extinction $[R \equiv A_v/E(B-V)]$ is well correlated with the level of UV extinction. Specifically, they find that lines of sight with larger R values exhibit smaller values of A_λ/A_v where $\lambda < 4000$ Å. In this paper, I explore the empirical chemistry of CH and H_2 with R for diffuse lines of sight with $\langle A_v \rangle \approx 1$ mag. I discuss in § II the source of the data and the statistics of the sample. In § III I present a comparison of the abundances of CH and H_2 as a function of R. Finally, I examine the observed results in terms of the processing of grains and differential photodestruction effects.

II. THE DATA

The abundance data discussed in this paper appear in Table 1 along with the relevant literature sources from which they were obtained. All of the H_2 data and most of the CH data come from the same set of authors. Since the approach of this paper is to examine the behavior of empirical chemistry with R, I view the internal consistency of the data set as an important factor. It is quite common to find systematic differences in abundances determined by different authors. Thus, I feel that comparing abundances derived in a consistent manner (i.e., by the same authors) reduces the relative uncertainties between different lines of sight to the general level of the intrinsic uncertainty in the data itself.

The values of R were derived by fitting near-infrared photometry obtained from the literature with the average curve of Rieke and Lebofsky (1985). This is the same technique employed by Clayton and Mathis (1988) and CCM and

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TABLE 1

OBSERVATIONAL DATA

Name (HD)	A_v	R	log N(CH)[a]	log N(H$_2$)[b]	log N(H I)[b]
2905.......	0.95	2.64	12.90	20.27	21.20
24398.......	0.89	2.70	13.34	20.67	20.81
24912.......	1.10	3.24	13.04	20.53	21.11
29647.......	3.80	3.60	14.20[c]	...	...
48099.......	0.95	3.52	12.57	20.30	21.15
112244.......	1.25	3.91	12.69	20.15	21.08
143275.......	0.68	3.60	12.34	19.42	21.10
144217.......	0.80	4.00	12.28	19.83	21.10
144470.......	0.83	3.75	12.51	20.04	21.20
145502.......	1.11	4.10	12.77	19.89	21.10
147165.......	1.50	3.80	12.49	19.79	21.30
147701.......	2.95	4.05	13.80[d]	...	...
147889.......	4.58	4.20	14.03[d]	...	...
147933.......	2.10	4.38	13.38[e]	20.57	21.54
148184.......	2.12	4.15	13.53[e]	20.63	21.15
149038.......	1.12	3.03	13.00	20.44	21.00
149757.......	0.99	3.09	13.40[e]	20.64	20.72
151804.......	1.52	4.11	12.70	20.26	21.08
164353.......	0.60	2.70	12.69	20.26	21.00
184915.......	0.74	2.86	12.94	20.30	20.90
193322.......	1.26	3.03	...	20.08	21.08
206165.......	1.34	2.79	13.36[f]	...	...
207198.......	1.71	2.76	13.65[f,g]	...	...
210839.......	1.65	2.95	13.34[f,g]	20.78	21.11
218376.......	0.75	3.00	12.88	20.15	20.95

[a] Federman 1982; Danks, Federman, and Lambert 1984; and Federman and Lambert 1988 unless otherwise noted.
[b] Bohlin, Savage, and Drake 1978.
[c] Crutcher 1985.
[d] Cardelli and Wallerstein 1986.
[e] Federman and Lambert 1988.
[f] Chaffee and Dunham 1979.
[g] Abundances redetermined by Federman and Lambert 1988.

involves a least-squares fit over the passbands R, I, J, K, and L between the average curve and the observed curve. The values of A_v were derived from the resulting best fit from which the values of R can be computed directly.

With the exception of five lines of sight, all of the lines of sight in Table 1 correspond to $A_v < 2$ mag and are considered diffuse (see § IIIa). In Table 2, I list the statistics of the sample for these diffuse lines of sight. The sample has been divided into two groups: $R < 3.5$ and $R > 3.5$. The significance of this will be seen in the next section. Table 2 shows that the statistics for the individual R subgroups are essentially identical to the entire sample as a whole so the two R subgroups statistically sample the same A_v and thus can be directly compared to one another.

TABLE 2

EXTINCTION STATISTICS FOR DIFFUSE CLOUDS WITH $A_v < 2$ MAGNITUDE

A_v Range	$\langle A_v \rangle$	n	σ	Notes
0.6–1.7..............	1.08	20	0.34	Entire sample
0.6–1.7..............	1.08	11	0.35	$R < 3.5$, $\langle R \rangle = 2.89$[a]
0.7–1.5..............	1.08	8	0.32	$R > 3.5$, $\langle R \rangle = 3.85$[a]
0.6–1.7..............	1.01	10	0.30	$R < 3.5$, $\langle R \rangle = 2.92$[b]
0.7–1.5..............	1.08	8	0.32	$R > 3.5$, $\langle R \rangle = 3.85$[b]

[a] Stars with CH data.
[b] Stars with H$_2$ data.

III. DISCUSSION

a) N(CH) and N(H$_2$) versus R

Diffuse clouds are generally considered to be regions transparent to UV radiation and are characterized by moderately low density and reddening. In terms of molecular chemistry, the use of the term *diffuse* line of sight takes on a more restricted definition. Diffuse clouds with measurable abundances of molecules such as CH typically have $A_v < 2$ mag and are characterized by densities of a few hundred particles per cubic centimeter (van Dishoeck and Black 1986; Prasad et al. 1986; Federman and Lambert 1988). The above definitions represent a crude transition from photochemistry to the regime where photoprocesses no longer dominate. From a model analysis of the chemistry of CH, CN, and C$_2$, Federman and Lambert (1988) suggest that the transition to the regime where gas-phase chemistry dominates may generally occur for clouds with $A_v > 2$ mag and log N(CH) ≥ 13.6, with lines of sight with lower column densities of CH being generally associated with the dominance of photochemical processes.

Using the above generalized definitions, I have defined the data in Table 1 characterized by log N(CH) < 13.6 and $A_v < 2$ mag as diffuse cloud lines of sight. Figure 1 shows, as filled squares, N(H$_2$)/A_v and N(CH)/A_v plotted against R. The open squares correspond to lines of sight with $A_v > 2$ mag and will be discussed later. I have divided the molecular column densities by A_v in order to remove, to first order, differences in column densities due to variable column lengths. If all of the diffuse lines of sight have similar *average* densities, then N(CH) and N(H$_2$) should scale *approximately* linearly (for small variations in A_v) with column length and A_v for the line-forming regions (i.e., for constant density, $N/A_v \approx$ constant). Of the 19 diffuse lines of sight with CH data, five stars show distances of $r > 1$ kpc, six show 600 pc $\leq r < 1$ kpc, and eight show $r < 600$ pc. For those stars with $r > 600$ pc, additional contributions to the reddening could arise from the foreground material outside of the molecular cloud region, making those points in Figure 1 lower limits. I assume, however, that the majority of the reddening arises in the molecular hydrogen region and that normalizing by A_v is statistically valid under the assumption of an average cloud density. However, plotting the CH and H$_2$ data without normalizing by A_v results in a nearly identical mean distribution but with a dispersion which is larger by ~ 0.06 in the log. I take this to imply that normalizing by A_v does in fact remove some variations due to differing column lengths. Note that the data in Table 1 give log $\langle N$(H I + 2H$_2$)$\rangle = 21.21 \pm 0.10$ for the $R < 3.5$ subgroup and 21.21 ± 0.07 for $R > 3.5$ subgroup (see Table 3).

At this point it is worth commenting on the potential biases between the two R subgroups for the stars with $A_v \approx 1$ mag. For the $R > 3.5$ group, five of the eight stars are in the Ophiuchus cloud, and one naturally wonders if the observed trends are the result of peculiarities associated with this unusual cloud region and are therefore bias. The answer to this is of course yes, but it seems that the "peculiarities" are associated with the larger R values, and are not restricted to the Ophiuchus cloud. The inclusion of three non-Ophiuchus stars in this group would seem to support this. In addition, the Ophiuchus star ζ Oph ($R = 3.09$) clearly shares the properties of the $R < 3.5$ subgroup. Also, in a CH versus CN diagram, these Ophiuchus stars show a distribution with respect to the model density limits of Federman and Lambert (1988) that is generally same as for the $R < 3.5$ subgroup. Finally, the
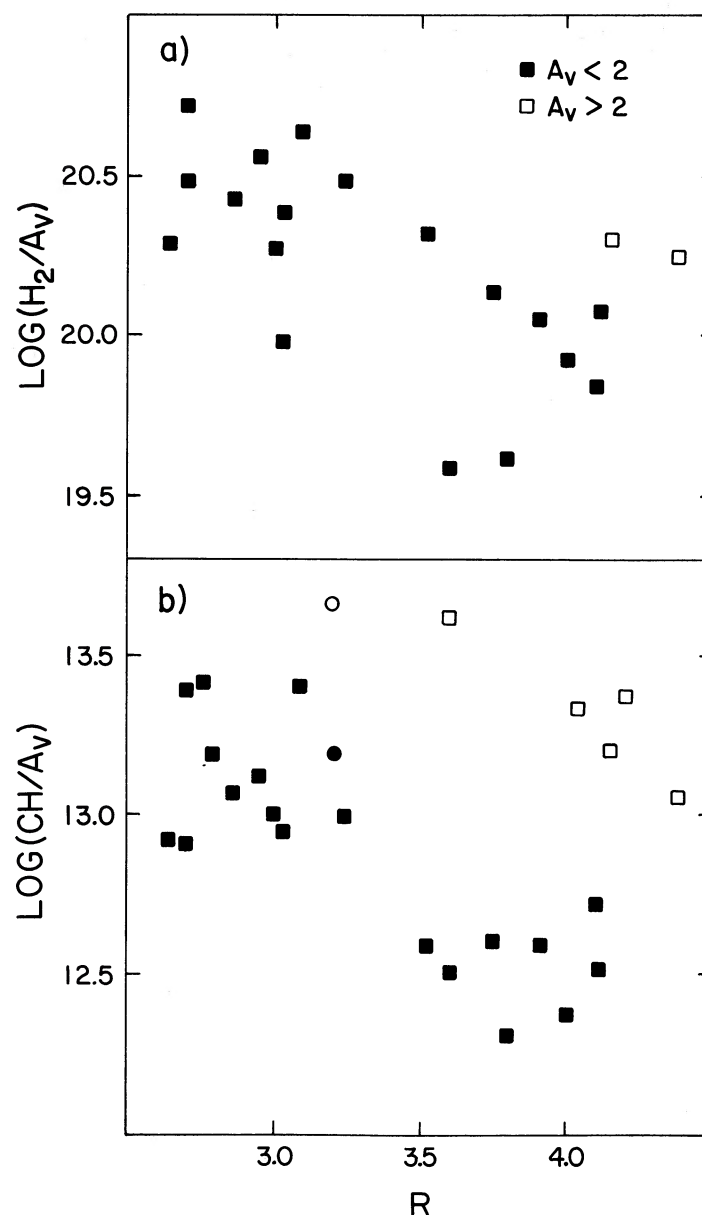
Fig. 1.—Logarithm of the column of (a) H_2 and (b) CH normalized by A_v. The filled squares represent the data defined as arising from diffuse clouds with $A_v < 2$ mag. The open squares correspond to lines of sight with $A_v > 2$ mag. The open and filled circles correspond to the largest and smallest column density of CH observed toward the Cep OB III cloud with $A_v = 2.18$ mag and 1.15 mag, respectively (Cardelli and Smith 1988).

general shape of the extinction curves for the Ophiuchus stars are no different than for other lines of sight with similar R values (CCM).

The most notable feature of Figure 1 is the well defined statistical behavior of the column densities of both H_2 and CH with R. The average abundance of both molecules clearly decreases as R increases. The fact that both show a similar slope dependence with R arises from the empirical result that $N(\mathrm{CH}) \propto N(H_2)$ (Federman 1982; Danks, Federman, and Lambert 1984).

Another way of presenting the data is shown in Figure 2 where the column densities of CH and H_2 are normalized by the total column density of hydrogen nuclei. From the notation of Spitzer (1976), the fraction of hydrogen nuclei contained in molecular hydrogen, $f(H_2) = 2H_2/(2H_2 + \mathrm{H\,I})$, is shown in Figure 2a. Similarly, one can also define the fraction of hydro-

gen nuclei contained in CH, $f(\mathrm{CH})$, which is shown in Figure 2b. As with Figure 1, there is a clear indication in Figure 2 that the relative abundance of CH and H_2 decreases as R increases. If one accepts the notion that variations in R are related to the processing of grains through variations in the size distribution, then Figures 1 and 2 imply that such processing directly effects the chemistry of CH and H_2. It should be stressed that while real variations in the local density and local radiation field (due to the proximity of bright stars) do exist for individual lines of sight, the discussion below is based upon the premise of *mean variations* of the sample.

b) Interpretation: Grain Processing and Photochemistry

Table 2 lists the statistics for the data in Table 1 defined to be diffuse cloud data. Because these data in Figure 1 appear to be naturally separated at $R \approx 3.5$, I have used this value to
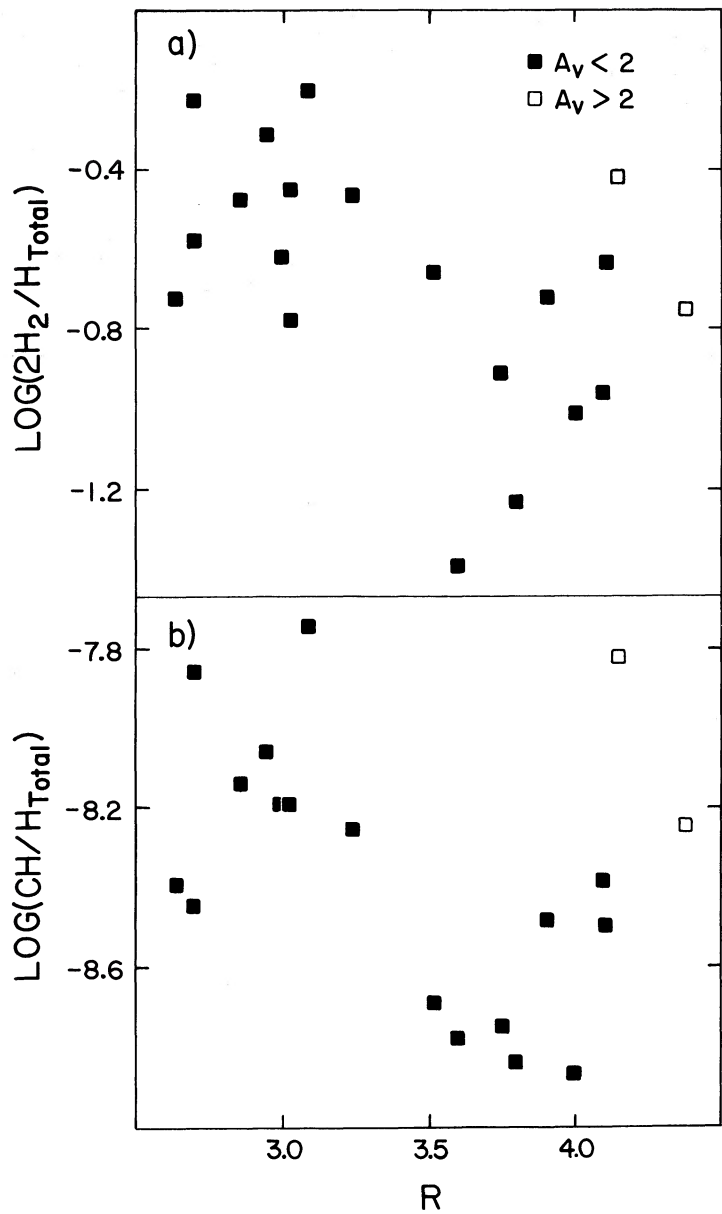
FIG. 2.—Logarithm of the (a) fraction of hydrogen nuclei contained in H_2 and (b) ratio of CH to the total hydrogen nuclei column density where $N_{total} = N(H\ I)$ + $2N(H_2)$. Again, the filled squares correspond to the diffuse cloud data with $A_v < 2$ mag while the open squares represent data with $A_v > 2$ mag.

TABLE 3

LOG ABUNDANCE STATISTICS FOR DIFFUSE CLOUDS WITH $A_v < 2$ MAGNITUDE

R^a	$\langle N(H) \rangle^b$	$\langle N(CH) \rangle$	$\langle N(H_2) \rangle$	$\langle N(CH)/A_v \rangle$	$\langle N(H_2)/A_v \rangle$	$\langle f(CH) \rangle$	$\langle 0.5f(H_2) \rangle^c$
<3.5	21.21	13.21	20.47	13.17	20.47	−8.05	−0.75
>3.5	21.21	12.57	20.03	12.55	20.01	−8.64	−1.17
Ratio^d	0.00	0.64	0.44	0.62	0.46	0.59	0.42

NOTE.—All of the data above are logarithmic values.

^{a} R subgroup (see Table 2).

^{b} log of the total hydrogen column density $\equiv \log [N(H\ I) + 2N(H_2)]$.

^{c} $0.5f(H_2) \equiv$ fraction of hydrogen molecules to total hydrogen nuclei.

^{d} log ratio of data for the two different R regions.

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divide the data into two R subgroups. As can be seen in Table 2, the two subgroups are nearly identical in terms of average A_v and dispersion. From this, one can define the values $\langle CH/A_v \rangle$ and $\langle H_2/A_v \rangle$, or $\langle f(CH) \rangle$ and $\langle f(H_2) \rangle$ for each R subgroup. These values are listed in Table 3.

Examination of Table 3 reveals that the average abundance of H_2 and CH has decreased by factors of 3 and 4, respectively, between the two R subgroups. Given that the mean conditions appropriate for these diffuse lines of sight are not dependent on R (i.e., the *mean* temperature and density is approximately the same for the two R subgroups), then the observed decrease in the molecular abundances can be attributed to a combination of changes in the formation and destruction rates with R. Because the chemistry of CH appears tied to the equilibrium abundance of H_2, I will first examine the above effects with respect to molecular hydrogen.

i) *Formation and Destruction of* H_2

Because radiative association of H atoms into H_2 is strongly forbidden (Watson 1975, chap. 5), H_2 is predicted to be formed on grain surfaces. Formation occurs at the rate $\zeta_g \propto S_g n(H)$ (Hollenbach, Werner, and Salpeter 1971; Jura 1974), where S_g is proportional to the total available surface area (Snow 1983) and $n(H)$ is the total density of hydrogen atoms. In regions exposed to UV photons, destruction arises through spontaneous radiative dissociation. The rate of photodestruction can be written as $\zeta_{pd} \propto \zeta_0 \exp(-\tau_{uv})\Sigma(L_i)$ where ζ_0 is the dissociation rate derived from the unattenuated radiation field (i.e.,

at the surface of the cloud), τ_{uv} is the attenuation optical depth due to dust near the absorption bands at ~ 1000 Å, and the term $\Sigma(L_i)$ is related to the excitation of H_2 through absorption of UV photons in the Lyman and Werner systems in the 912–1100 Å range. This term is important because it includes the effects of excitation and self-shielding of H_2 and is therefore a function of depth in the cloud (van Dishoeck 1986a).

Recent work of CCM has shown that there is a strong correlation between total-to-selective extinction, R, and the level of UV extinction. They provide an analytic formula, good for $\lambda < 0.3$ μm, of the form $\langle A_\lambda/A_v \rangle = a(\lambda^{-1}) + b(\lambda^{-1})/R$. From their analytic fits, extinction curves can be predicted which are in relatively good agreement with the observations. In particular, the results show that $\langle A_\lambda/A_v \rangle$ decreases as R increases. Thus, for a given A_v, the radiation field seen by a cloud increases, through a decrease in τ_{uv}, as R increases. Figure 3 shows, in A_λ/A_v, the difference between an extinction curve with $R = 2.9$ and $R = 3.9$ derived from the analytic formula of CCM. The actual dispersion of radiation into a cloud will depend upon the relative albedo and phase function of the grains (e.g., Sandell and Mattila 1975; Roberge, Dalgarno, and Flannery 1981) and may be a function of R. However, since I am considering only the global effects of the relative reduction in extinction, one can write $\tau_{1000} \approx a_{1000} A_{1000}$, where A_{1000} is the extinction at 1000 Å and a_{1000} is a dimensionless attenuation scale factor and is assumed to be independent of R.

Based on lines of sight in Ophiuchus, Jura (1980) argued that substantial increases in R over the average value are the result
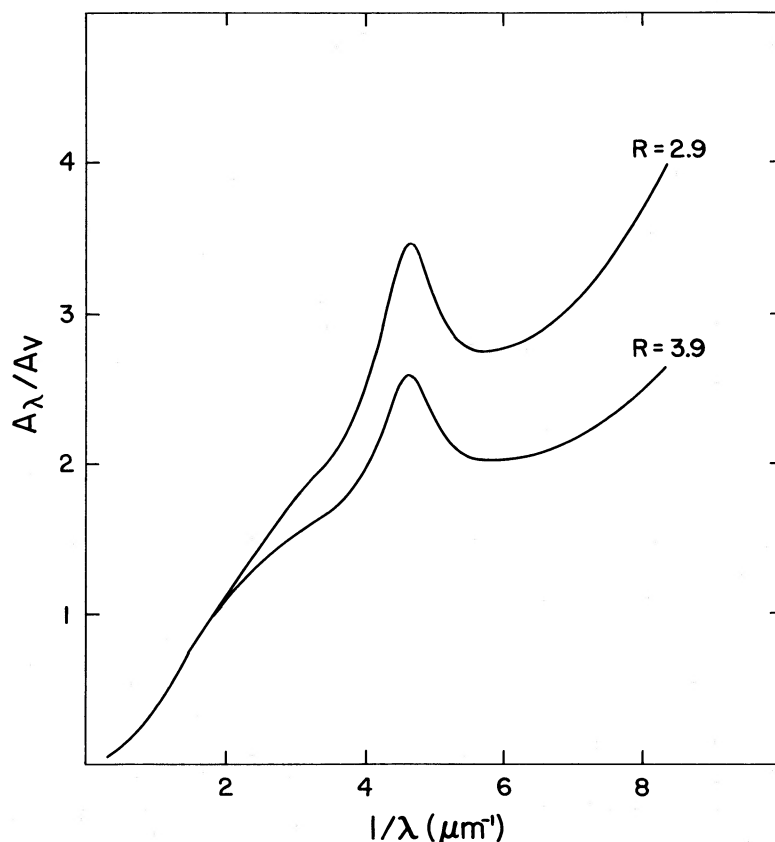

FIG. 3.—Relative extinction curves, in units of A_λ/A_v, appropriate for total-to-selective extinction values of $R = 2.9$ and 3.9. The results have been obtained using the analytic formula of Cardelli, Clayton, and Mathis (1988) and represent the average extinction appropriate for the two R subgroups discussed in the text. Note that for the larger R subgroup, the lower extinction curve will result a cloud seeing a larger incident radiation field than for smaller values of R.

of grain growth through coagulation. Snow (1983) concluded that coagulation of grains can result in a loss of total grain surface area per unit volume by as much as a factor of 2–3 for lines of sight like ρ Oph ($R \approx 4.4$). Consequently, Snow concluded that the effective grain formation rate of H_2, S_g, will suffer a similar decrease. Thus, as R increases, one might expect a subsequent decrease in the efficiency of H_2 formation.

If I start by making the assumption that the dependence of the term $\Sigma(L_i)$ with R is small and ignore self-shielding by H_2 for the two R groups [this latter assumption may be weak since there is evidence that self-shielding may become important for $\log N(H_2) > 14$ (van Dishoeck 1987a)], then I can construct the following ratio;

$$\frac{[n(H_2)/n_H]_{R \approx 2.9}}{[n(H_2)/n_H]_{R \approx 3.9}} \propto \frac{(\zeta_g/\zeta_{pd})_{R \approx 2.9}}{(\zeta_g/\zeta_{pd})_{R \approx 3.9}}$$

$$\propto \frac{[S_g/\exp(-\tau_{1000})]_{R \approx 2.9}}{[S_g/\exp(-\tau_{1000})]_{R \approx 3.9}}$$

$$\propto \frac{[S_g(R \approx 2.9)/S_g(R \approx 3.9)]}{\exp(\Delta\tau_{1000})} \qquad (1)$$

where $n_H \equiv 2n(H_2) + n(H)$, and $\Delta\tau_{1000}$ is the difference between the attenuation optical depth at 1000 Å for $\langle R \rangle \approx 3.9$ and 2.9. Again, I note that the attenuation of the radiation field is not directly proportional to the observed extinction, but is a radiative transfer problem involving specific "properties" of the observed extinction (e.g., pure absorption and the albedo and phase function of the grains). However, if I (cautiously) assume that the relative contributions of absorption and scattering do not change significantly with R, then $\Delta\tau$ can be estimated from the extinction curves, where $\Delta\tau_{1000} \approx a_{1000}(\Delta A_{1000})$. Using $a_{1000} \approx 0.63$ (Hollenbach, Werner, and Salpeter 1971) and the results of CCM (Fig. 3) extrapolated to 1000 Å, I find that for $A_v \approx 1$ mag, $\Delta\tau_{1000} \approx -1.0$ yielding $2.7[S_g(R \approx 2.9)/S_g(R \approx 3.9)]$ for equation (1). If the relative grain formation rate has decreased by a factor of 2 because of the coagulation of small grains, I find that the ratio of the abundance of H_2 between the $R \approx 2.9$ and $R \approx 3.9$ group is about a factor of 5, or 0.7 dex. Examination of Table 3 shows that this change has the proper sign but is about a factor of 1.7 larger than is observed. Given the statistical nature of the analysis and the simple assumptions made above, I find this result to be in relatively good agreement. Because the physics of coagulation is rather complex and the resulting factors such as grain shape, mean density (Mathis 1988), and charge are uncertain, it is possible that the reduction in total surface area is overestimated. However, if some degree of self-shielding is appropriate for both R subgroups (van Dishoeck 1987a) such that some fraction of the total column density is found in a protected cloud "core," then the effectiveness of the photodestruction term in equation (1) is reduced. In this case, a larger portion of the observed decrease in $N(H_2)$ with R can be attributed to a change in R_g.

ii) Formation and Destruction of CH

Independent of the relative contribution of the above processes to the reduction of H_2, CH will be similarly reduced because its formation is tied to the equilibrium abundance of H_2 through the initial reaction $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ followed by the ion-molecule reaction $CH_2^+ + H_2 \rightarrow CH_3^+ + H$ and the dissociative electron recombination of CH_2^+ and CH_3^+ leading to CH (Black and Dalgarno 1973; Black Dalgarno,

and Oppenheimer 1975; van Dishoeck and Black 1986). Examination of Table 3 reveals an additional decrease in the mean abundance of CH relative to H_2 of the order 0.20 in the log for the two R subgroups. Admittedly, this decrease is relatively small when compared to the dispersion of the data. However, as can be seen in Table 3, this decrease is present even when the samples are handled in three different ways. I therefore consider this decrease to be real.

With the notation of Federman (1982) and Federman and Lambert (1988), the steady state rate equation can be written as;

$$\frac{N(CH)}{N(H_2)} \approx \frac{0.67k_5\,n(C^+)}{\zeta_{pd}(CH) + k_3\,n(C^+)}, \qquad (2)$$

where k_5 and k_3 are rate constants, $n(C^+)$ is the density of ionized carbon, and the term $\zeta_{pd}(CH)$ represents the photodissociation rate for CH. Because photodissociation of CH arises from both absorption into predissociation states and directly into the continuum for 3500 Å $> \lambda > 1200$ Å (Solomon and Klemperer 1972; Barsuhn and Nesbet 1978; van Dishoeck 1987b), the wavelength dependence of $\zeta_{pd}(CH)$ must be considered. (I have not included the effects of photoionization which appear to be smaller than photodissociation by about a factor of 6 for $A_v = 1$ mag [Draine and Katz 1986].) If the wavelength dependence is included, $\zeta_{pd}(CH)$ can be expressed as $\Sigma_\lambda k_{pd}(\lambda) \exp(-a_\lambda A_\lambda)$, where $k_{pd}(\lambda)$ represents the wavelength-dependent photodestruction terms, A_λ is the extinction, and a_λ is the dimensionless attenuation scale factor such that $a_\lambda A_\lambda$ corresponds approximately to the true attenuation, τ_λ. In the absence of dust, values for $\zeta_{pd}(CH) = \zeta_0(CH) = \Sigma_\lambda k_{pd}(\lambda)$ depend upon the assumed unattenuated radiation field and typically range from 8×10^{-10} s^{-1} to 1.3×10^{-9} s^{-1} (Barsuhn and Nesbet 1978; van Dishoeck 1987a, b; Federman and Lambert 1988). I adopt the results of van Dishoeck (1987b) which yield $\Sigma_\lambda k_{pd}(\lambda) \approx 9.5 \times 10^{-10}$ s^{-1} and which are in good agreement with Barsuhn and Nesbet (1978).

Adopting $k_{pd}(\lambda)$ from van Dishoeck (1987b), A_λ (for $A_v \approx 1$) from CCM (see Fig. 3), $a_\lambda = $ constant ≈ 0.5 and independent of R, $n(C^+) = 2.5 \times 10^{-4}n$, and k_3 and k_5 from Federman and Lambert 1988, $N(CH)/N(H_2)$ can be expressed as a function gas density for the two R subgroups. The expression for $n(C^+)$ accounts for a factor of 2 depletion of carbon which is typical for diffuse environments (Cardelli 1984). For $\langle n \rangle \approx 300$ cm^{-3} I find $\log[N(CH)/N(H_2)_{R=2.9}]/[N(CH)/N(H_2)_{R=3.9}] \approx 0.12$. For $\langle n \rangle \approx 100$ cm^{-3} and 500 cm^{-3}, I find the above ratio equals 0.15 and 0.10, respectively. Increasing or decreasing a_λ by 0.2 changes the above results by at most a few hundreths.

On the basis of these crude estimates and their good agreement with the actual measured mean decrease from Table 3 (≈ 0.18), it is possible that we are seeing the effects of additional photodissociation of CH with increased R. However, it should be pointed out that the above estimates may be only lower limits since I have used the same depletion factor for both R subgroups. Regions in which larger than normal R values are observed (e.g., the Ophiuchus cloud) often tend to be associated with larger than normal gas depletions. Use of an additional factor of 2 depletion of carbon for the $\langle R \rangle \approx 3.9$ increases the above results by ~ 0.25 dex for $\langle n \rangle \approx 300$ cm^{-3} and hence depletion can be an important factor. However, there are a number of stars in our $\langle R \rangle \approx 2.9$ sample that show elemental depletions, including carbon, that are larger than

normal and similar to the depletions seen toward the $\langle R \rangle \approx 3.9$ group (Morton 1975; Snow 1975, 1984; Snow and Joseph 1985). If depletion depends primarily on cloud density (Snow 1975), then one might not be too surprised to find similar mean carbon depletions for the two R subgroups. The fact that the two groups are separated in R may be related to the past history of the grains in denser environments, the results of which are still maintained in the current lower density clouds. In particular, additional depletion of carbon for the larger R subgroup in past, higher density environments may have been selectively reduced because of the larger incident UV flux (synonymous with larger R values) in the current environments. However, I cannot totally dismiss the possibility that enhanced depletion of carbon for the larger R subgroup has contributed significantly to the decrease in the abundance of CH (Black 1988).

Regardless of the difficulty in assessing past history, it is a certainty true that at the present time, the diffuse lines of sight with larger R values are "seeing" a selectively larger incident UV flux, the consequences of which can be amply used to explain a smaller CH/H_2 ratio through increased photodestruction of CH.

c) Lines of Sight with $A_v > 2$ mag

For lines of sight with $A_v > 2$ mag, significant reduction in the UV radiation field from shielding by dust occurs, even for larger than normal R values. Consequently, photodestruction processes become less significant (Federman and Lambert 1988). Unfortunately, with the exception of two stars (χ Oph and ρ Oph), H_2 data are not available for lines of sight in the sample with $A_v > 2$ mag and so I cannot examine the H_2 chemistry for these more reddened lines of sight. However, CH data do exist for these lines of sight which are plotted as open symbols in Figure 1b. Although the dispersion in A_v is much larger than for the $A_v < 2$ sample and direct comparison is difficult, the data do seem to also show a general decrease in N(CH) with increasing R.

Because of the empirical relationship between CH and H_2, it is tempting to imagine that a similar trend also exists for $N(H_2)$. While higher levels of photodestruction probably exists for the larger R lines of sight (i.e., UV radiation penetration into the cloud will be greater for larger R), this will probably be applicable only to the outer portions of the clouds since attenuation and shielding will greatly reduce the radiation field deep in the cloud. Of course, adjustments must be made in equation (2) to account for both increased depletion of carbon and the general decrease of $n(C^+)$ through recombination in these denser environments. However, because of the lower relative UV extinction, one might expect that the larger R lines of sight will have larger relative $\langle n(C^+) \rangle$ which would only serve to enhance N(CH) relative to the smaller R lines of sight. In any case, lack of good data on the depletion of carbon makes any definitive statement impossible. If larger depletions of carbon exist in the interior of the larger R clouds, then a decrease in N(CH) could result.

The apparent persistent decrease of N(CH) with increasing R might be a reflection of an intrinsic defect in the formation rate of H_2. As discussed by Snow (1983), reduction in the formation rate of H_2 due to loss of grain surface area through coagulation associated with increasing R will persist and perhaps increase deep inside dense clouds shielded from UV radiation. The trend shown in Figure 1b may be a reflection of this. This can be seen from equation (1) if one assumes that the photodestruction term is negligible (the destruction term would be replaced by the dissociation rate appropriate for cosmic rays). As a result, the production of H_2 will be controlled mainly by the available grain surface area.

IV. CONCLUSIONS

The analysis presented here has focused on the empirical relationship between the abundances of CH and H_2 and their dependence on variable UV extinction in diffuse clouds with $A_v < 2$ mag. I have utilized the recent results of CCM, who have shown that the UV extinction relative to A_v is well correlated with the value of total-to-selective extinction, R. In particular, they find $\langle A_\lambda/A_v \rangle$ decreases as R increases. Using a generalized approach which has centered on the mean variations in N(CH) and $N(H_2)$ with R, I have found that the abundances of CH and H_2 decrease for lines of sight with larger R values. From this I conclude the following.

1. The decrease in the abundance of H_2 for larger than normal R values occurs through a combination of reduction in formation rate via a reduction in available grain surface area and an increase in photodestruction via a decrease in UV dust extinction.

2. The abundance of CH relative to H_2 decreases for larger R through increased photodestruction.

3. The decrease of N(CH) and probably $N(H_2)$ appears to persist for lines of sight with $A_v > 2$ mag where photoprocesses are probably negligible, possibly indicating that grain modification plays an important role in the formation of H_2 and other molecules dependent upon H_2 in clouds where gas-phase chemistry dominates.

While UV extinction parameters are necessary for the detailed chemical modeling of interstellar clouds, these data are often nonexistent or difficult to obtain. The results presented here and in CCM suggest that R could be employed as a variable parameter in such modeling. It is of interest to note that variation in the UV radiation scaling factor, I_{uv}, between different lines of sight used in the model results of van Dishoeck and Black (1986) are consistent with the R-dependent results presented. In addition, variations in the ratio of observed/model predictions for CN (Federman and Lambert 1988) for some lines of sight might be explained via variations in R.

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