MOLECULAR FORMATION IN HOT DIFFUSE CLOUDS

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Abstract. A description is given of the processes of molecular forma-
tion and destruction in diffuse interstellar clouds and detailed models
of the clouds lying towards ζ Ophiuchi, ζ Persei and o Persei are used
to assess the validity of gas phase chemistry. Modifications that may
arise from shock-heated regions are discussed.

Diffuse clouds are local concentrations of interstellar gas that
do not obscure entirely the light from the stars which lie behind
them and they may be studied observationally by measuring the absorp-
tion of the starlight by the individual constituents of the cloud
(cf. Snow 1979). The systems CO, C^+, CH and OH have been studied also
by measuring their emission in the radio region of the spectrum (cf.
Knapp and Jura 1976, Crutcher 1977, 1979, Lang and Willson 1978, Liszt
1979). Because diffuse clouds are simpler astrophysical entities than
are the dense molecular clouds where star formation occurs the study of
diffuse clouds provides a more stringent assessment of the molecular
formation and destruction processes which occur in the interstellar
gas. However, the chemistry of diffuse clouds is modified substantially
by photodissociation and photoionization processes and is not always
free of the complicating influence of interstellar shocks.

In this brief review I will attempt to summarize recent progress
in our knowledge of the processes involved in diffuse cloud chemistry
and draw attention to areas of significant uncertainty. I will not
discuss the formation of the most abundant molecule, H_2, except to
note that at low temperatures H_2 is formed by association on the sur-
faces of grains in a reasonably well understood way (cf. Hollenbach
and McKee 1980) although we cannot predict with confidence the initial
rotational and vibrational distribution of the newly created molecules
(cf. Hunter and Watson 1978), an uncertainty which affects the analysis
of the observed rotational populations of H_2 and the calculation of the
associated heating rate.

At high gas temperatures, found in shocked regions and in ionized

nebulae, associative detachment (cf. Dalgarno and McCray 1973)

$$H + H^- \rightarrow H_2 + e \tag{1}$$

may be a significant source of H_2 (cf. Black 1978) which leads to an emission spectrum containing lines from highly excited vibration – rotation levels (Bieniek and Dalgarno 1979). The spectrum is characteristic and its observation would be a powerful diagnostic probe of the mechanism of associative detachment and of the environment in which it occurs.

Given the formation of H_2 all the other molecules detected in diffuse clouds can be explained by gas phase mechanisms. In the proposed chemical schemes the reactions are initiated by cosmic rays or by ultraviolet photons. Cosmic ray ionization of H and H_2 produces H^+ ions which undergo charge transfer with atomic oxygen:

$$H^+ + O \rightarrow H + O^+ \tag{2}$$

The resulting O^+ ions react with H_2 initiating an abstraction sequence which terminates in the production of H_3O^+. The H_3O^+ ions recombine dissociatively to create OH and H_2O in unknown proportions. In diffuse clouds, H_2O is photodissociated to give OH and essentially every H^+–O charge transfer leads to OH.

The absolute fluxes are based upon a rate coefficient for reaction (2) of $5 \times 10^{-10} \exp(-232/T)$ cm^{3}s^{-1} inferred from an analysis of OH abundances measured towards ζ Oph (Black and Dalgarno 1977). A study by de Boer (1979) of atomic oxygen towards ζ Oph (Morton 1975) indicates that the abundance of atomic oxygen should be increased by a factor of three. The inferred rate coefficient of reaction (2) is reduced correspondingly to a value of $1.7 \times 10^{-10} \exp(-232/T)$ cm^{3}s^{-1}, in harmony with calculations (Chambaud et al. 1979) which can be represented approximately by $1.5 \times 10^{-10} \exp(-232/T)$ cm^{3}s^{-1}.

There remain uncertainties in the depletion factor of carbon (cf. Liszt 1979) and in the OH destruction rates but it is unlikely that the derived fluxes are in error by more than a factor of three.

There has been a marginal detection of H_2O (Snow and Smith 1979, Snow 1979) at about the 2σ level. With the oscillator strength measured by Smith, Yoshino and Parkinson (1979), the implied abundance is 2.65×10^{13} cm^{-2}. The calculated abundance is 2×10^{12} f cm^{-2} (Black and Dalgarno 1977) where f is the fraction of dissociative recombinations which lead to H_2O. According to Herbst (1978), f is less than 0.5 and may be as small as 0.1. The discrepancy between theory and observation is large and probably cannot be accommodated by changes in molecular rate coefficients or model parameters. If the detection of H_2O is real, a new source of H_2O must be sought.

Cosmic ray ionization of H^+ also leads to HD through the sequence

$$H^+ + D \rightarrow H + D^+ \tag{3}$$

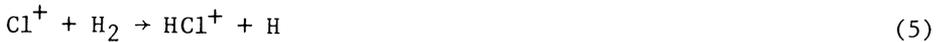$$D^+ + H_2 \rightarrow HD + H^+ \tag{4}$$
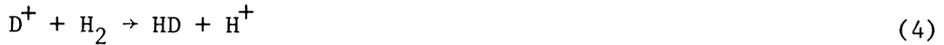
(Black and Dalgarno 1973a, Watson 1973). Accurate values of the rate coefficient of (3) have been presented by Watson et al. (1978) It is of interest to note that the existence of H_2 is the strongest evidence of the importance of grain chemistry and the existence of HD is the strongest evidence of the importance of gas phase chemistry.

The abundance of HD is directly proportional to the cosmic ray flux and the cosmic (D)/(H) abundance ratio. The cosmic ray fluxes have been inferred from the OH abundances so that (D)/(H) may be inferred from the HD abundances. For ζ Oph, ζ Per and o Per the ratio is 1.4×10^{-5} to within the considerable HD observational uncertainties (Hartquist, Black and Dalgarno 1978), a value in harmony with the mean for distances up to 200 pc from the Sun (York and Rogerson 1976). The general agreement lends support to the postulated OH and HD chemistries.

The chemistry can be tested also by observations of CO which is formed as a consequence of the C^+-OH and C^+-H_2O reactions and destroyed mainly by photodissociation. A comparison of theory and observation is presented in table 1. A photodissociation rate which reproduces the CO abundance measured for ζ Oph is successful in the ζ Per and o Per clouds also.

Of the constituents ionized by ultraviolet photons, only Cl^+ reacts chemically with H_2 (Jura 1974, Dalgarno et al. 1974). The sequence of

$$Cl^+ + H_2 \rightarrow HCl^+ + H \tag{5}$$

$$HCl^+ + H_2 \rightarrow H_2Cl^+ + H \tag{6}$$

and

$$H_2Cl^+ + e \rightarrow HCl + H \tag{7}$$

leads to HCl. Hydrogen chloride is destroyed by photodissociation and by reaction with C^+ according to

$$HCl + C^+ \rightarrow CCl^+ + H \tag{8}$$

(Dalgarno and Black 1976). For ζ Oph, Black and Dalgarno (1977) predict a column density of 1.0×10^{13} cm^{-2}. An upper limit to the equivalent width of the absorption line at 1290 Å has been obtained by Wright and Morton (1979) which is consistent with a column density of 1.3×10^{12} cm^{-2} when the oscillator strength measured by Smith, Yoshino and Parkinson (1979) is used. The discrepancy is at least an order of magnitude. It could be resolved by a decrease in the

interstellar photoionization efficiency of Cl (Jura and York 1978) or
by postulating an activation energy for reaction (5) (Black and
Smith 1979).

Of greater fundamental importance to interstellar chemistry is
the reaction of C^+ with H_2. In a cold gas, C^+ does not react
chemically with H_2. Radiative association

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \qquad\qquad (9)$$

may occur (Black and Dalgarno 1973b), initiating a sequence which
produces CH and CH^+ and, through a reaction scheme suggested by Watson
(1973), also C_2 (Dalgarno and Black 1976), C_2H and $C_2H_2^+$. The mole-
cules C_2H and $C_2H_2^+$ are important in chemical schemes for the formation
of the complex molecules found in dense clouds.

The rate coefficient of the initial step, reaction (9), is a
critical parameter. The measured abundance of CH towards ζ Oph can
be reproduced with a rate coefficient of 5×10^{-16} cm^3 s^{-1}, a value
which is successful also for the direction towards ζ Per and o Per,
as table 1 illustrates.

Table 1
Column densities log N (cm^{-2})*

	ζ Oph		ζ Per		o Per	
	Obs	Th	Obs	Th	Obs	Th
CO	15.0–15.2	15.0	14.7–15.0	15.0	14.7–15.0	15.1
CH	13.5–13.6	13.6	13.0–13.4	13.6	13.4–13.6	13.5
CN	12.94	12.95	12.6	12.5	12.3–12.7	11.9
C_2	12.9	12.9	13.1	13.1	–	13.3
CH^+	13.0	11.4	12.2	11.5	12.7	11.5

*References to the observational data are given by Snow (1979)

The interstellar molecule CN is produced by various reaction
sequences involving atomic nitrogen and the CH cycle. In table 1,
the predicted abundances are compared with measurements. The photo-
dissociation rate of CN has been slightly modified to achieve precise
agreement between theory and measurement for ζ Oph. There is a small
discrepancy for o Per which may be due to an overestimate of the
nitrogen depletion; the [N]/[H] ratio, measured by Snow (1976), is
unusually small.

Molecular carbon, C_2, is produced by reactions of C^+ with the
CH cycle. Its existence in about the correct abundances (cf. table 1)
was predicted (Black and Dalgarno 1977, Black et al. 1978) before
its detection (Lutz and Souza 1977, Snow 1978, Hobbs 1979, Chaffee
et al. 1979). The importance of C_2 as a probe of the interstellar
environment has been discussed by Lutz and Souza (1977) and by Chaffee
(1979).

The chemical scheme fails to predict the measured abundances of CH^+ (cf. table 1). It can be made to work by the simple expedient of increasing the rate coefficient of reaction (9) to about 10^{-14} cm^3s^{-1} (Black, Dalgarno and Oppenheimer 1975), a value that is consistent with the current estimate based upon a combination of theory (Herbst, Schubert and Certain 1977) and laboratory measurement (cf. Fehsenfeld 1979). The scheme then predicts too much CH, CN and C_2. There is sufficient arbitrariness in the mechanisms forming and destroying CN and C_2 that the predicted overabundances may not be significant. That for CH could be remedied either by assuming that CH_2 preferentially undergoes dissociative ionization rather than photodissociation or that the reaction

$$CH^+ + H_2 \rightarrow CH_2^+ + H$$
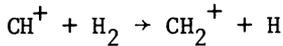
becomes slow at low temperatures.

If the postulated rate coefficient of about 5×10^{-16} cm^3S^{-1} is correct, an additional source of CH^+ is necessary. In a hot gas, the endothermic reaction

$$C^+ + H_2 \rightarrow CH^+ + H$$
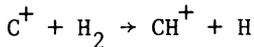
can proceed, and provided the gas remains hot long enough, a substantial amount of CH can be created The high temperature diminishes the destruction by dissociative recombination (Mitchell and McGowan 1978) and the resulting abundance may depend more upon the efficiency of photodissociation (Kirby et al. 1979, Kirby 1979) and, because of the reverse of (11), on the concentration ratio of atomic and molecular hydrogen.

Elitzur and Watson (1978,1979) have suggested that the hot gas is produced by a shock resulting from the expansion of an H II region around the parent star and they have developed a quantitative model which gives fair agreement with the measured abundances with plausible choices of the shock velocity and the pre-shock densities of H_2 and H. The alternative suggestion has been made by de Jong (1979) that the hot gas is located at the exterior boundary of the cloud where it is heated by interstellar shocks driven by supernovae. This model would help to explain some anomalies in the measured populations of high rotational levels of H_2 (Hartquist and Dalgarno 1980). Collision-induced dissociation may not have been taken into account correctly in these shock models (Dalgarno and Roberge 1979).

Gas phase chemistry is radically altered in a hot gas (Iglesias and Silk 1978, Elitzur and de Jong 1978, Hartquist, Oppenheimer and Dalgarno 1980). Endothermic reactions with H_2 play a dominating role and the H_2/H concentration ratio is a critical parameter. Molecular ions such as SiH^+, SH^+, NaH^+, MgH^+, FeH^+ and HCl^+ may be formed and survive long enough to be detectable. An upper limit of 2×10^{11} f_a cm^{-2} where f_a is the absorption oscillator strength, has been obtained by

Jenkins et al. (1973) for the column density of the molecular ion MgH^+ towards ζ Oph. A laboratory determination of f_a might be valuable in assessing the significance of shocked gas, though the Mg depletion may be severe in the molecular cloud (Snow and Meyers 1979).

Neutral molecules are readily produced in heated gas. Depending upon the extinction of the radiation field, the density of the heated gas and the cooling rate of the gas, large abundances of OH and H_2O (Iglesias and Silk 1978, Elitzur and de Jong 1978, Elitzur 1979) and of SH and H_2S (Hartquist et al. 1980) can result. If confirmed, the tentative detection of H_2O (Snow 1979) would be strong evidence of a shocked region and the earlier conclusion about gas phase chemistry and cosmic ray ionizations would require revision.

I remarked earlier that the abundances of all the molecular species detected in diffuse clouds can, with the exception of H_2, be attributed to gas phase. The agreement may in fact be illusory stemming in large part from the considerable uncertainties in our knowledge of the multiplicity of molecular processes that occur.

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DISCUSSION FOLLOWING DALGARNO

Glassgold: A long-standing problem in chemical modelling of diffuse clouds is the fairly large uncertainty in the total gaseous abundances of carbon and oxygen. How do you deal with this situation?

Dalgarno: The uncertainties in the depletion directly affect the calculated molecular abundances.

Solomon: The division between "dense clouds" and diffuse clouds may in some cases be arbitrary. The star which is observed optically or in the UV may be on the edge of a very large dense molecular cloud. For example Omicron Persei is on the edge of a molecular cloud extending for at least 25 parsecs (see Barrett et al., this conference), so that what appears as a "diffuse cloud" is in reality a small part of a dense molecular cloud. The chemistry observed in the optical or UV may reflect the recent past of the molecular cloud, and result in part from the interaction of the OB star with the cloud.

Dalgarno: The cloud models have a high density core, and for ζ Oph

and o Per the derived radiation field is substantially larger than the interstellar radiation field, suggesting that the clouds are close to, and probably physically associated with the stars.

Huntress: The radiative association rate constant for $C^+ + H_2$ is strongly dependent upon temperature. What temperature are you using for the clouds where you have used the value $5 \times 10^{-16} cm^3/s$ for this rate constant?

Dalgarno: In the core of one cloud, T=22K and in the cores of the other two T=45K. We used $5 \times 10^{-16} cm^3 s^{-1}$ for all three clouds.

D. Smith: You have stressed that your chemical models of diffuse clouds predict a lower concentration of CH^+ than is observed. We have recently shown in a laboratory study that the atom reactions $C_2H^+ + N$, $C_2H_2^+ + N$ and $C_2H^+ + O$ generate CH^+ ions (rate coefficients $\sim 10^{-10} cm^3 s^{-1}$ at 300K). Could these reactions significantly increase the CH^+ concentration and so narrow the gap between prediction and observation?

Dalgarno: The reactions are of considerable interest. Their inclusion will lessen but not remove the discrepancy.

Herbst: The reactions $CH^+ + H_2 \rightleftarrows CH_2^+ + H$ are nearly thermoneutral. The backward reaction should be studied in the laboratory as an additional CH^+ source.

Dalgarno: The reaction and its inverse are indeed critical to the CH^+ formation scheme.

Huntress: The new value for the heat of formation of CH^+ does considerably reduce the exothermicity of the $CH^+ + H_2$ reaction. It is possible therefore that this reaction may be temperature dependent so the rate constant at 20-40 K could be considerably smaller than the measured value at 300 K. Would a smaller rate constant for this loss process relieve the long-standing problem of the predicted CH^+ densities in diffuse clouds?

Dalgarno: Yes.

Elitzur: If the high H_2O abundance toward ζ Oph is correct, then the pre-shock density for the CH^+ calculation can be increased. H_2O represented the most severe constraint on the pre-shock density since it can be produced in abundance behind the shock.

Dalgarno: I agree.

de Jong: Could you elaborate on the remark you made that collisional destruction rates of molecules in interstellar shocks may be quite a bit smaller than has been assumed up to now?

Dalgarno: The laboratory values are appropriate to high densities. In interstellar shocks, radiative stabilization is a significant process which can drastically decrease the rate of collision-induced dissociation, depending on gas density and on the particular molecule. Preliminary estimates of collision-induced dissociation rates for H_2 and CO, which take radiative stabilization into account, are given by Dalgarno and Roberge (Ap. J.(Letters) 233, L25, 1979).