INTERSTELLAR MOLECULES – THEORY

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Abstract. A number of possible mechanisms for the formation of molecules in the interstellar medium are discussed. Plausible suggestions have been made for the production of most of the known diatomics, but there is little understanding of polyatomics so far.

Over the last two decades a number of possible mechanisms for formation of molecules in the interstellar medium have been proposed. Until recently attention was focussed entirely on diatomic molecules because until December 1968 no serious consideration was given to polyatomic molecules.

The classical study by Bates and Spitzer (1951) was concerned with radiative recombination of atoms, in particular

$$C + H \rightarrow CH + h\nu,$$
$$C^+ + H \rightarrow CH^+ + h\nu.$$
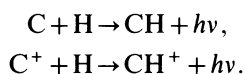
These processes were dismissed as too slow under interstellar conditions to account for the observed amounts of interstellar molecules. More recently Solomon and Klemperer (1972) have reconsidered these and other radiative recombinations. By including the effect of 'atomic-multiplet trapping' from the higher components of ^3P and ^2P states of C and C^+, the effect of quantum-mechanical tunnelling through the centrifugal barrier and by using revised values for oscillator strengths of the molecular transitions they obtained rates that make it plausible that in H I regions with H atom densities $\geqslant 10$ cm^{-3} a rich mixture of diatomics will be produced, including CH, CH$^+$, CO, CN, C$_2$ and C$_2^+$. Reactions such as

$$CH^+ + O \rightarrow CO + H^+,$$
$$CH^+ + N \rightarrow CN + H^+,$$
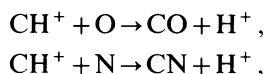
are important in yielding interstellar CO and CN. Their work was primarily aimed at clouds of moderate density such as those between us and ζ Ophiuchi.

In the meantime various people (Kahn, 1955; McCrea and McNally, 1960; Gould and Salpeter, 1963; Hollenbach and Salpeter, 1971; Knaap *et al.*, 1966) studied in increasing detail the feasibility of formation of H$_2$ from H on the interstellar dust grains.

Aannestad (1973) has presented elaborate calculations combining radiative recombination, dust grains and shock waves in an apparently all-embracing theoretical treatment of interstellar molecule formation.

Other mechanisms of molecule formation that have been proposed include formation in the dense atmospheres of stars with subsequent expulsion into the interstellar medium (Herbig, 1970), or by photolysis of molecules within the mantles of dust grains to produce free radicals and, subsequently, more complex molecules (Green-

berg *et al.*, 1972). However the former proposal has to include regular production of molecules to balance the steady removal of molecules by condensation on grains (Rank *et al.*, 1971) and the molecules require constant protection by dust grains from the rapid photolysis that would be produced by the average interstellar UV radiation field (Stief *et al.*, 1972). The mantle photolysis mechanism has not yet been developed to the quantitative stage for comparison with observed molecular abundances. Most recently the formation of interstellar molecules from negative ions has been proposed by Dalgarno and McCray (1973).

The overall picture that emerges is the following:

(i) The only plausible mechanism proposed so far for the formation of H_2 in cool interstellar clouds (e.g., $T = 50$ K, $n_H = 100$ cm^{-3}, $\tau_v = 1$) is on interstellar grain surfaces. However at higher temperatures the alternative mechanism (Dalgarno and McCray):

$$e + H \rightarrow H^- + h\nu,$$
$$H^- + H \rightarrow H_2 + e,$$
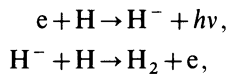
becomes increasingly important, both because catalysis by grains becomes less effective and also because the rate of formation of H^- becomes greater.

(ii) In 'young' clouds ($\sim 10^7$ yr) CO, CH$^+$, CH and CN are next most readily formed (essentially as analysed by Solomon and Klemperer) but, in older clouds (say $> 5 \times 10^7$ yr) OH and later NH become more abundant, being produced by recombination on grain surfaces that have grown considerably in size in the ageing cloud. The calculations of OH abundance by Aannestad for a cloud of 500 $M_\odot$ and a depletion factor $d(C^+) = 0.1$ are compatible with observation. The observations on the clouds in front of ζ Ophiuchi can also be accounted for reasonably if the clouds are assumed to be young.

Aannestad (1973) has also attempted to evaluate the chemical effects of shock waves that occur when clouds collide or when they encounter expanding H II regions; he published typical results as a function of time after passage of the shock front. The most abundant molecules surviving for some time ($>$ a few hundred years) after the shock are (after H_2) CO, CN and CH in that order.

Thus we are left with a picture that the formation and rough relative abundances of H_2, CO, CN, CH, CH$^+$ and probably OH in interstellar clouds can be accounted for by invoking the intervention of interstellar grains as catalysts for a variety of reactions. However, a formidable array of input data, most of it soft, is involved in the calculations, making it hard to assess the confidence limits for the final results.

The situation for the other observed polyatomic molecules is more obscure. Aannestad noticed that his model did not easily account for observed abundances of H_2CO. Dalgarno and McCray have suggested that a number of polyatomic molecules could plausibly be formed by negative ion radiative attachment (Table I). No specific calculations on these mechanisms were offered and they must be regarded at present as interesting armchair galactochemistry. We might especially note the presence of a mechanism for formation of NO with a rate very similar to that of the preceding reaction for water formation. Searches for NO have so far been unsuccessful (1970).

TABLE I

Negative ion radiative
attachments
(Dalgarno and McCray,
1973)

$H^- + CO \rightarrow HCO + e$
$H^- + HCO \rightarrow H_2CO + e$
$O^- + CH_2 \rightarrow H_2CO + e$
$CH_2^- + O \rightarrow H_2CO + e$
$O^- + H_2 \rightarrow H_2O + e$
$O^- + N \rightarrow NO + e$
$O^- + CS \rightarrow OCS + e$
$S^- + CO \rightarrow OCS + e$
$S^- + H_2 \rightarrow H_2S + e$
$CH^- + N \rightarrow HCN + e$
$CN^- + H \rightarrow HCN + e$
$CH_2 + S^- \rightarrow H_2CS + e$
$CH_2^- + HCN \rightarrow CH_3CN + e$

While no persuasive quantitative theory of formation of polyatomic molecules has been published, there are a number of factors that have to be incorporated in a successful theory. We note that the studies of Stief *et al.* (1972) imply that the molecules must be formed within the photolytic protection of dust clouds of at least moderate opacity.

Firstly no cyclic molecules have been found (Table II), although in some cases integration to very low noise levels has been performed. While all of these molecules contain more atoms than any molecule yet found (the smallest is aziridine C_2H_5N) one wonders whether the mechanism of formation makes ring formation highly unlikely. Chemically there is a better prospect of producing ring structures by reactions on surfaces of catalysts than by reactions in the gas phase and so there may be a

TABLE II

Some cyclic molecules for
which searches have been
negative (Sgr B2)

Molecule	Limiting noise (peak to peak) (K)
Aziridine	0.01[a]
Pyrrole	0.02[a]
Imidazole	0.02[a] 0.08[b]
Pyrazole	0.04[a]
Pyridine	0.05[a]
Furan	0.08[b] 0.03[c]

[a] Parkes 64-m
[b] Green Bank 43-m
[c] Hat Creek 26-m

hint here that the larger molecules are formed in gas phase reactions. We might also note in passing that pyridine is a constituent of the bis pyridyl magnesium tetrabenz porphine that Johnson (1970) has proposed as the absorber of the diffuse interstellar lines.

Secondly molecules with N bound to O have not been detected, yet two molecules containing both N and O have been found: HNCO and $H-C\diagup_{\diagdown NH_2}^O$. Solomon and Klemperer (1972) have shown that NO does not form by radiative recombination but it is hard to see why NO bonds should be avoided on, for example, grain surfaces. Incidentally we have recently had a search for HNO at Parkes without success. One would have thought $O+NH$, or perhaps $O^-+NH \rightarrow HNO+e$, are plausible.

Finally some of the polyatomic molecules that have been detected are known to chemists as highly reactive. I especially instance thioformaldehyde H_2CS and methanimine H_2CNH. The formation of such species in low temperature gas reactions is understandable but one is a little uneasy about catalytic formation of such species. One would expect them to undergo further rapid reactions on the grain surface to yield more chemically stable species.

This then seems to me to be the present state of understanding of molecule formation – plausible suggestions for production of most of the known diatomics but no real understanding of polyatomics. Hopefully, further observations, positive and negative, will provide a stronger fabric from which galactochemists will fashion a more wearable account of the origin of interstellar molecules.

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DISCUSSION

Robinson: Brown has drawn attention to the absence of molecules with the NO combination. There is also no known case of a carbon-carbon double bond, as pointed out by Winnewisser. The absence of NO and C=C may provide useful clues to the mechanisms of molecule formation.

Turner: The calculations by Aannestad, based on the Solomon-Klemperer theory, have been shown to be irrelevant by recent work by Smith, Lizst and Lutz (*Astrophys. J.* **183**, (1973), 69) and by Yoshimine, Green and Thaddeus (*Astrophys. J.* **183**, (1973), 899), which shows that the direct radiative recombination rates of CH^+ and CH are much lower than previously assumed. Further, Julienne and Kraus (in M. A. Gordon and L. E. Snyder (eds.), *Molecules in the Galactic Environment*, John Wiley and Sons, New York, 1973) have shown that *indirect* radiative recombination (inverse predissociation) proceeds at comparable or larger rates under interstellar conditions, and since this process favours a different set of molecules (CN, CO, OH) than the direct process, relative abundances would be predicted quite differently to those of Aannestad.

The probable formation mechanism is *positive* ion-molecule reactions in gas phase, as studied by Herbst and Klemperer (*Astrophys. J.* **185**, (1973), 505) and by Watson (*Astrophys. J. Letters* **181** (1973), L129, and **183** (1973), L17). Such reactions proceed with much larger rates than those involving negative ions (Dalgarno and McCray, *Astrophys. J.* **181** (1973), 95). Such reactions will operate over a wide range of cloud densities, including the tenuous clouds ($A_v \sim 2$–3 mag) where molecules are seen optically, and the 'black' clouds ($A_v \sim 200$ mag) where complex molecules are seen at radio wavelengths. In these latter clouds, surface reactions cannot operate (cf. Watson and Salpeter, *Astrophys. J.* **174** (1972), 321 and **175** (1972), 659), and positive ion-molecule reactions (initiated by cosmic ray ionization) appear to be the only formation processes whose rates exceed or at least are comparable with the rate of destruction of molecules by permanent adsorption onto grain surfaces.

Certain points of comparison, of a qualitative nature, may be made between predicted abundances, via positive ion-molecule reactions, and observed abundances. One is that these processes favor formation of molecules with unsaturated carbon bonds (cf. Turner, *J. Roy. Astron. Soc. Canada* (1974), in press) and discriminate against saturated bonds. This agrees with observation. Another is that these processes predict that OH abundances should be independent of total density, if OH is destroyed primarily by absorption onto grains. This also agrees with observation (Turner, in *Galactic and Extragalactic Radio Astronomy*, Springer-Verlag, New York, 1973; Turner and Heiles, *Astrophys. J.* (1974), in press). Qualitative predictions are useful, because these do not depend on calculational difficulties associated with unknown reaction rates, or omission of reactions, difficulties which affect attempts at quantitative predictions in all theories of molecular formation.

In summary, arguments can be made against all interstellar formation mechanisms proposed to date except positive-ion molecule reactions, which predict correctly certain qualitative observational aspects, and which have yet to be thoroughly tested in a quantitative sense.

Brown: Mechanisms of formation based on homogeneous gas-phase positive ion-molecule reactions are particularly attractive since there is a better chance of developing a thorough quantitative theory than one could hope for in the case of heterogeneous reactions. However, until the articles by Herbst and Klemperer and Watson have been published and subjected to full scrutiny by scientists it is difficult to comment further.

Donn: The ζ Oph cloud is rather anomalous. The high dispersion work of Hobbs shows that four clouds are present. The CH^+ line differs in velocity from other species. It is therefore dangerous to use this region as standard for comparing theoretical and observed molecular abundance calculations.

The interstellar clouds are characterized by extreme deviations from thermodynamic equilibrium. The use of laboratory reaction rates requires a Boltzmann distribution for molecular vibrational and rotational levels. Chemical techniques now are beginning to yield rates for specific initial energy states and these may differ considerably among themselves and from equilibrium values. It is therefore also dangerous to use laboratory data for interstellar calculations without great care.

Brown: It is very dangerous to go to the literature and take an expression that chemists have derived for the rate of a reaction just by studies at room temperature and above. When activation energies and frequency factors obtained from experimental data at room temperature are used to predict reaction rates at low temperatures very sizeable errors can result – perhaps one or more orders of magnitude.

Morimoto: Nakagawa and others calculated relative production rate of molecules on the grain surfaces assuming that atoms chemically absorbed on the grain surface move on the surface until they form a molecule and leave the surface. This gives large production rates for molecules found astronomically

(plus those without dipole moment) including polyatomic molecules. (Nakagawa, *Pub. Astron. Soc. Japan* (1974), in preparation).

Brown: The simple model used by Nakagawa *et al.* could point to some interesting possibilities for further study. However, rates of heterogeneously catalyzed reactions are often enormously affected by details of the surface structure of catalysts and so the assumptions employed by Nakagawa *et al.* must be regarded with reserve.

Parijskij: I would like to inform you that an experimental approach to molecular formation is in progress at the Institute of Physics and Technique in Leningrad. Conditions in cold and dense clouds were simulated, and a great amount of large molecules were visible in their mixture.