

INTERSTELLAR MOLECULES FROM COOL STARS*

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1. Introduction

Problems relating to the formation of interstellar molecules have assumed an enhanced importance in recent years mainly because of the detection of a variety of molecular species in interstellar space. The interstellar molecules CH, CH⁺, CN were discovered several decades ago by their characteristic bands in optical stellar spectra, while OH, H₂O, H₂CO, HCN, HC₃N, NH₃ and CO were detected during the past few years by their spectral features in the radio waveband. The optical detection of interstellar H₂ was reported only several weeks ago.

In addition to molecules in the gaseous state it is likely that several molecular species exist in the form of solid particles. The possible existence of ice particles composed of H₂O, NH₃, CH₄ has been discussed for many years (van de Hulst, 1946), but there is yet no definite identification of these materials (Danielson *et al.*, 1965; Knacke *et al.*, 1969). On the other hand recent infrared data have indicated the presence of silicate material (presumably MgSiO₃) in the Trapezium region of M42 (Ney and Allen, 1969) and in clouds surrounding certain cool stars (Woolf and Ney, 1969). There is also evidence from the ultraviolet extinction curve of starlight to indicate the presence of graphite particles in interstellar space (Stecher, 1965 and 1970; Hoyle and Wickramasinghe, 1969). A wide range of observational data relating to the interstellar dust particles may be explained by the hypothesis that grains are a mixture of graphite, silicate and iron particles (Hoyle and Wickramasinghe, 1969; Wickramasinghe, 1969; Wickramasinghe and Nandy, 1970). Graphite particles could arise from cool carbon stars in the manner originally suggested by Hoyle and Wickramasinghe (1962), and iron and silicate particles may arise in a similar manner from cool oxygen-rich giant stars (Gilman, 1969). In addition to these particles, which probably form the main content of solid interstellar matter, it is likely that other solid materials – notably, SiC, CaO, Al₂O₃, TiO – exist in trace quantities. In dense, dark interstellar clouds we may expect gaseous volatile molecules to be condensed as mantles on refractory solid particles.

Molecule formation processes discussed so far fall into two main categories: (a) radiative association, (b) reactions occurring on grain surfaces. In the present paper I shall discuss the possibility that the cool flow of matter from the atmospheres of red giant stars may constitute an additional source of some interstellar molecules. This process was discussed by Stecher and Williams (1966) in relation to the production of interstellar H₂. The mechanism envisaged here involves the formation of molecules and solid particles under thermodynamic conditions in stellar atmospheres and their subsequent expulsion into interstellar space by radiation pressure.

2. Molecular Equilibrium in a Stellar Atmosphere

Molecular abundances in the atmosphere of a cool giant star may be computed on the assumption of thermodynamic equilibrium. At densities in the range 10^{16} – 10^{12}

TABLE I

Element	C-rich case (i)	O-rich case (ii)
H	1.0	1.0
N	1.0×10^{-4}	1.0×10^{-4}
C	5.0×10^{-3}	5.0×10^{-4}
O	1.0×10^{-3}	1.0×10^{-3}
Si	4.0×10^{-5}	4.0×10^{-5}
Mg	3.5×10^{-5}	3.5×10^{-5}
S	1.5×10^{-5}	1.5×10^{-5}
Fe	1.0×10^{-5}	1.0×10^{-5}

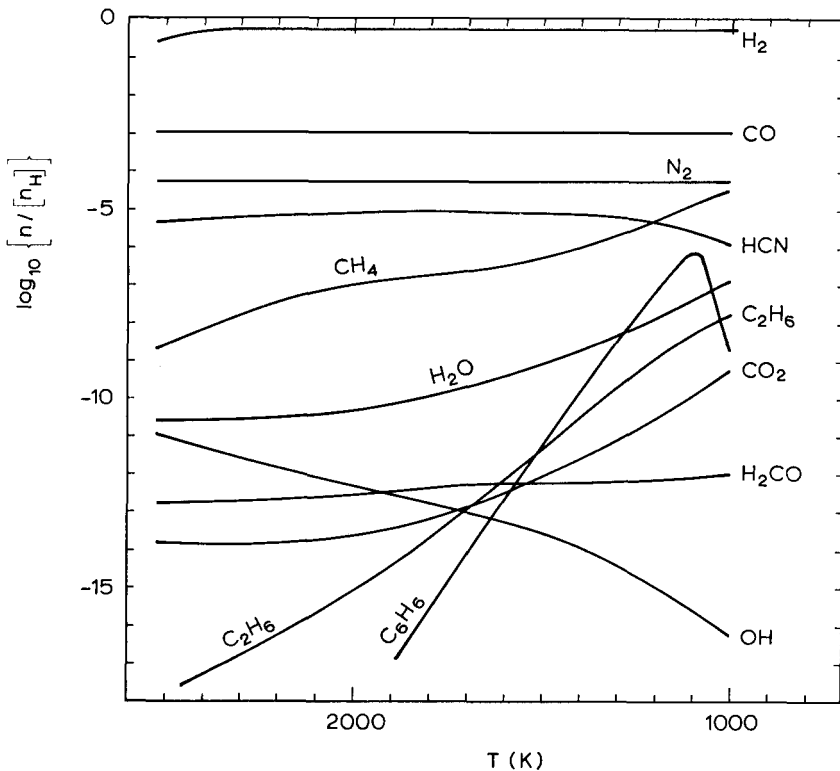


Fig. 1. Molecular abundances in carbon star atmospheres. Abundances are computed relative to the total hydrogen density ($[n_H] \approx 10^{15}$) and plotted as functions of T . Condensation of graphite occurs at $T \lesssim 2200$ K. The molecular abundances plotted for these temperatures are those in equilibrium with bulk graphite. At $T \approx 1000$ K the mass fraction of graphite condensed under thermodynamic conditions was found to be $\sim 79.9\%$.

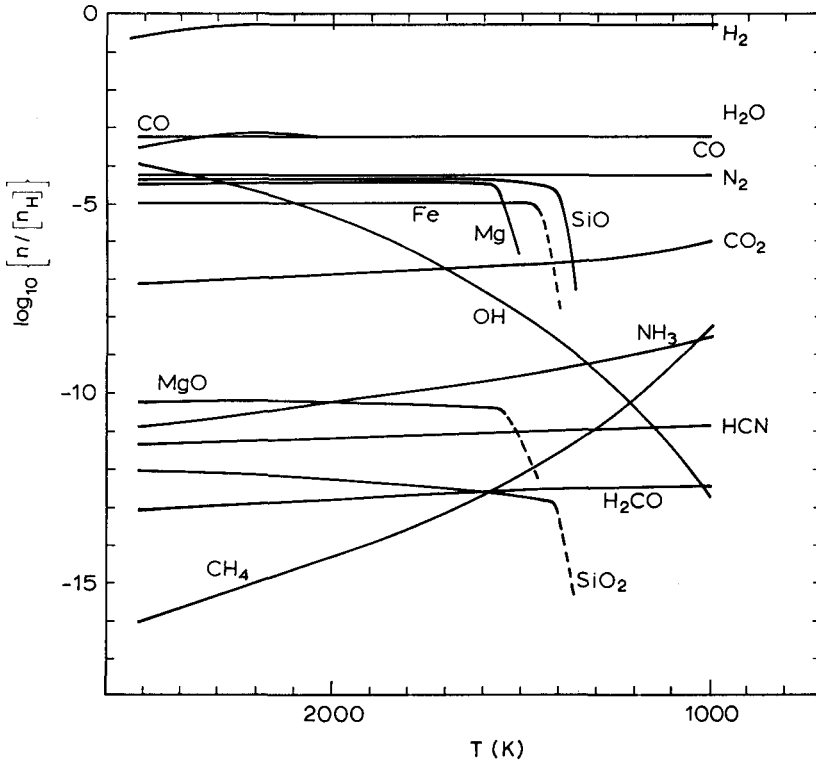


Fig. 2. Molecular abundances in Mira-type stellar atmospheres as functions of temperature. Abundances are computed relative to the total hydrogen density. The dashed segments of the curves for Fe, MgO and SiO₂ indicate that the solid phase has formed and is in equilibrium with the gaseous component at the temperatures indicated. The condensation of MgO and SiO₂ at approximately the same temperature may result in the formation of MgSiO₃ rather than separate particles of MgO and SiO₂. The condensation of a particular metal whether as an oxide, silicate or in free form is followed by a sharp drop in the concentrations of all molecular species involving this metal. At $T \approx 1000$ K it was found that essentially all the available Fe, Mg and Si are in condensed form under thermodynamic conditions. The value of $[n_{\text{H}}]$ is taken to be 10^{15} cm^{-3} .

cm^{-3} and temperatures in the range 3000–1000 K, appropriate for the atmosphere of a cool star, chemical equilibrium conditions are established very rapidly – in time-scales less than 10^3 sec in most cases. Molecular equilibria for stellar atmospheres were originally computed by H. N. Russell in 1934. More extensive calculations using modern thermochemical data were subsequently carried out by Hoyle and Wickramasinghe (1962, 1968), by Tsuji (1964) and by Gilman (1969).

Two types of cool star may be distinguished in the present context: (i) carbon stars with $\text{C}/\text{O} > 1$ whose spectra are dominated by bands of C₂, CN, CH etc., and (ii) Mira-type stars with $\text{C}/\text{O} < 1$ whose spectra show bands of TiO and ZrO. Both stellar types are irregular variables with periods of the order ≈ 1 yr and effective temperatures varying in the range 2000–3000 K. The gas phase abundances of various molecular species have been computed for the two sets of relative abundances set out

in Table I, case (i) being appropriate to carbon stars and case (ii) to Mira-type stars. The results for these two cases with a total hydrogen density $[n_{\text{H}}] \approx 10^{15} \text{ cm}^{-3}$ are set out in Figures 1 and 2 (see also Figure captions). About 60 molecular species and several refractory solids were included in the calculations. In the case of carbon stars we find that the bulk of C in excess of O condenses as graphite particles at temperatures below 2200 K. This could occur close to the photospheric layers of the star at minimum phase. In the case of Mira-type stars the chief condensates are found to be MgSiO_3 and Fe and condensation occurs at $T \approx 1500 \text{ K}$. In addition to these materials solid particles of CaO , Al_2O_3 , TiO may condense in a region of the atmosphere where the temperature is in the range 1200–1000 K (Wickramasinghe, 1968). Such low temperatures may not occur in the photospheric region even at minimum phase, but could occur in the outer layers of the stellar atmosphere where the gas density has fallen only a few powers of ten below the photospheric value. In Table II we set out

TABLE II

Molecule	Case (i) No. per condensed C	Case (ii) No. per condensed Mg
H_2	1.3×10^2	1.6×10^4
H_2O	3.3×10^{-5}	1.6×10^1
CO	2.5×10^{-1}	1.6×10^1
OH	1.4×10^{-14}	6.4×10^{-9}
H_2CO	1.8×10^{-10}	1.3×10^{-8}
CH_4	7.1×10^{-3}	1.2×10^{-4}
NH_3	1.7×10^{-5}	8.5×10^{-5}
N_2	1.3×10^{-2}	1.6
HCN	1.6×10^{-3}	4.0×10^{-8}
C_2H_6	3.0×10^{-6}	—

the calculated abundances of the principal molecular species for the two cases referred to above with T set equal to 1000 K and $n_{\text{H}} \approx 10^{15} \text{ cm}^{-3}$. The abundances are given relative to the smeared out number density of condensed C atoms in case (i) and relative to the smeared out number density of condensed Mg atoms in case (ii). In the carbon-rich case the bulk of oxygen is tied up as CO, hydrogen as H_2 and nitrogen as N_2 . In addition to simple molecules a variety of more complicated hydrocarbon molecules may exist in the thermodynamic mixture. In the oxygen-rich case the bulk of carbon is in the form CO, oxygen as H_2O , nitrogen as N_2 and hydrogen as H_2 . These conclusions are quite insensitive to the assumed value of the gas density; nor are they sensitive to the precise values chosen for the relative elemental abundances. At temperatures much below 1000 K the gas densities may be too low for the establishment of equilibrium conditions in timescales $\leq 10^7$ sec. Thus $\sim 1000 \text{ K}$ may be a reasonable estimate for the temperature at which equilibrium relative concentrations of molecules become effectively 'frozen in' to effluent material from cool stars.

3. Expulsion of Dust by Radiation Pressure

The expulsion of dust by radiation pressure could be accompanied by the release of an appreciable fraction of the gaseous atmosphere in which the grains are embedded (Wickramasinghe *et al.*, 1966). The radiation force on a dust particle of radius a is given by

$$F = Q_{pr}\pi a^2 \frac{L}{4\pi R^2 c} \cong Q_{pr}\pi a^2 \frac{\sigma T_{\text{eff}}^4}{c} \quad (1)$$

where Q_{pr} is the efficiency factor for radiation pressure, L , R , T_{eff} are respectively the luminosity, radius and effective temperature of the star. The gravitational attraction of the grain to the star is

$$G = g \left(\frac{4}{3}\pi a^3 s\right) \quad (2)$$

where g is the surface gravity $\approx 1 \text{ cm sec}^{-2}$, and s is the density of grain material. The ratio

$$\frac{F}{G} \approx \frac{3Q_{pr} \times 10^{-2}}{gas} \approx 10^3 - 10^4 \quad (3)$$

with $Q_{pr} \approx 1$ for grains of radii $a \cong 10^{-5} - 10^{-6} \text{ cm}$, so that radiation pressure can equalise the gravitational attraction of a mass $\approx 10^3 - 10^4$ times that of grains.

In a region of a stellar atmosphere where the condensation of either graphite or silicates is complete the ratio of the masses of gas to dust is $\approx 10^3$. Thus we find that radiation pressure acting on the grains can cause the expulsion of essentially the entire region of grain condensation provided the grains and gas are sufficiently strongly coupled. For particle sizes of the order of $\approx 10^{-6} \text{ cm}$ and for gas densities exceeding 10^{12} cm^{-3} this coupling is most likely to exist, the terminal drift velocities of grains through gas being very strongly sub-sonic.

4. Injection of Molecules from Stars

The rates of ejection of gaseous molecules into interstellar space may now be computed if we assume that all the molecules present in the region of grain formation escape into interstellar space, being carried along with the dust. Since the mass of gas is $\sim 10^3$ times that of dust this assumption would appear to be valid in view of our preceding remarks. We further assume that the main sources of interstellar dust are cool stars and that the mass densities of graphite and silicates are comparable, each being equal to $\approx 10^{-26} \text{ g cm}^{-3}$ (Hoyle and Wickramasinghe, 1969). Since the mean lifetime of a refractory grain is $\tau \approx 10^9 \text{ yr}$ the rates of injection of C and Mg atoms in the form of graphite and silicates are

$$\frac{dn_C}{dt} \cong \frac{10^{-26}}{A_C m_H \tau} \approx 5 \times 10^{-13} \text{ cm}^{-3} \text{ yr}^{-1} \quad (4)$$

$$\frac{dn_{\text{Mg}}}{dt} \cong \frac{10^{-26}}{A_{\text{MgSiO}_3} m_H \tau} \approx 6 \times 10^{-14} \text{ cm}^{-3} \text{ yr}^{-1} \quad (5)$$

where A_C , A_{MgSiO_3} stand for the chemical atomic weights of graphite and $MgSiO_3$. The corresponding rates of injection of molecules of a given species M may now be computed from Table II and Equations (4) and (5) according to

$$\frac{dn_M}{dt} = \frac{dn_C}{dt} \left(\frac{n_M}{n_C}\right)_{(i)} + \frac{dn_{Mg}}{dt} \left(\frac{n_M}{n_{Mg}}\right)_{(ii)} \tag{6}$$

where $(n_M/n_C)_i$, $(n_M/n_{Mg})_{ii}$ are the molecular ratios in cases (i) and (ii). The resulting rates of enrichment of the interstellar medium in various molecular species is set out in the second column of Table III. The third column gives estimated values for the

TABLE III

	Injection rate from stars, $cm^{-3} yr^{-1}$	Estimated lifetime, yr	Equilibrium density, cm^{-3}
N_2	$\sim 10^{-13}$	$\sim 10^8$	$\sim 10^{-5}$
H_2	$\sim 10^{-9}$	$\sim 3 \times 10^2$	$\sim 3 \times 10^{-7}$
CO	$\sim 10^{-12}$	$\sim 10^4$	$\sim 10^{-8}$
H_2O	$\sim 10^{-12}$	$\sim 10^4$	$\sim 10^{-8}$
CH_4	$\sim 3 \times 10^{-15}$	$\sim 10^4$	$\sim 3 \times 10^{-11}$
HCN	$\sim 10^{-15}$	$\sim 10^4$	$\sim 10^{-11}$
NH_3	$\sim 10^{-17}$	$\sim 10^4$	$\sim 10^{-13}$
C_2H_6	$\sim 10^{-18}$	$\sim 10^4$	$\sim 10^{-14}$
H_2CO	$\sim 10^{-21}$	$\sim 10^4$	$\sim 10^{-17}$
OH	$\sim 3 \times 10^{-22}$	$\sim 10^4$	$\sim 3 \times 10^{-18}$

mean lifetimes τ_M of the molecules in a standard interstellar radiation field. The last column gives the equilibrium interstellar densities of these molecules computed from the two preceding columns by the relation $n_M = dn_M/dt \times \tau_M$. Non-negligible densities of N_2 , H_2 , H_2O , CO are seen to arise. Although the abundance of OH resulting directly from this process is very low, a somewhat higher value could result from the photodissociation of H_2O molecules ejected from stars.

5. Comparison with Grain Surface Reaction Yields

The optimum rate of formation of molecules AB on grain surfaces may be computed on the assumption that the reaction $A + B \rightarrow AB$ is exothermic and that the grain temperatures are sufficiently low to permit long residence times of adsorbed atoms. For a total mass density of grains of $\sim 2 \times 10^{-26} g cm^{-3}$ and mean grain radius of $\sim 10^{-5} cm$ the total grain surface per cm^{-3} is

$$\frac{2 \times 10^{-26}}{4/3\pi a^3 s} 4\pi a^2 \approx 3 \times 10^{-21} cm^2 per cm^3 \tag{7}$$

with the density of grain material $s \approx 2 g cm^{-3}$. If $n_A \leq n_B$ the rate of molecule for-

mation per cm^{-3} is

$$(3 \cdot 10^7) n_A v_{th} (3 \times 10^{-21}) \approx 10^{-8} \frac{n_A}{n_H} n_H \text{ cm}^{-3} \text{ yr}^{-1} \quad (8)$$

with v_{th} set equal to 10^5 cm^{-1} . For the relative abundances set out in the last column of Table I and for $n_H \approx 1 \text{ cm}^{-3}$ this gives $\approx 10^{-8} \text{ cm}^{-3} \text{ yr}^{-1}$ for H_2 , $\approx 10^{-12} \text{ cm}^{-3} \text{ yr}^{-1}$ for N_2 , $\approx 10^{-11} \text{ cm}^{-3} \text{ yr}^{-1}$ for CO and OH . These values are in excess of the corresponding stellar ejection rates set out in Table III by at least an order of magnitude. It thus appears that the stellar injection process provides only a relatively minor contribution to diatomic molecules in the general interstellar medium. The situation for more complex molecules is rather difficult to assess. From Figure 1 it is clear that appreciable quantities of complex molecules such as C_2H_6 , C_6H_6 may exist in a carbon star atmosphere at temperatures below $\sim 1000\text{K}$. As we have already pointed out cool stars are most likely to be the major sources of interstellar silicates, graphite and iron particles. They may also supply the interstellar medium with a wide range of polyatomic hydrocarbon molecules of varying degrees of complexity.

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