

THE CHEMICAL COMPOSITION OF INTERSTELLAR MOLECULAR CLOUDS

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Abstract. Relative abundances for molecules observed by radio astronomical techniques have been determined for several interstellar regions with differing physical properties.

INTRODUCTION

Lists of known interstellar molecules have been given in recent reviews by Winnewisser (1981) and Irvine (1983). In the present paper it is instead our intention to tabulate quantitative molecular abundances in several interstellar sources. It is obvious that such abundances are a necessary prerequisite to any real understanding of interstellar chemistry and its possible relationship to chemical evolution and the origin of life. Previous analyses have either dealt with a very restricted number of species or have utilized data necessarily drawn from a variety of investigators using different instrumentation (e.g., Brown and Rice, 1981; Turner and Thaddeus, 1977). This raises a number of calibration problems, among the most serious of which is that different observations may sample different size regions of the source. In the present article we draw extensively on the results of the recently completed "spectral scan" of the Orion molecular cloud and the envelope around the evolved star IRC+10216 carried out at the Onsala Space Observatory in Sweden (Johansson et al., 1983). These data provide the first consistently calibrated, very broad bandwidth millimeter wavelength spectra for astronomical sources. In order to extend the range of physical conditions considered, however, we do also include results for cold dark clouds such as TMC-1; in these cases we have been careful to compare only results obtained with similar spatial resolution and have attempted to avoid uncertainties due to radiative transfer

effects by use of data obtained for rare isotopic variants (Irvine and Hjalmarson, 1983; Hjalmarson and Irvine, 1983).

When considering the chemical compositions specified in the next section, it is well to bear in mind the selection effects inherent in the observational technique. First of all, since relevant kinetic temperatures are typically ≤ 100 K, the molecules observed are normally in the ground electronic and vibrational state. Thus, only pure rotational transitions are excited. An immediate restriction on observable species is then the requirement for a permanent electric dipole moment, which is lacking in such symmetric but potentially important molecules as N_2 , O_2 , CH_4 , and the symmetric hydrocarbons. Although in principle abundances of such species may be inferred from observations of chemically related molecules (e.g., N_2H^+), isotopic variants which do possess a permanent dipole moment ($^{16}O^{18}O$, CH_3D), or from vibrational transitions close to luminous energy sources such as embedded stars, results obtained to date are quite sparse. Other problems related to excitation concern the light hydrides such as H_2O , NH_2 , and CH_2 , whose pure rotational transitions occur primarily in the largely unexplored submillimeter region. Moreover, as J. M. Greenberg discusses at this Conference, at least some complex organic molecules are very likely tied up in the interstellar grains, so that their rotational spectra are unobservable and precise identification becomes difficult or impossible (the amount of such organic material is a subject of considerable controversy; see, for example, Whittet, 1981). A given molecular species can only be sought astronomically if its rotational spectrum is known, and at present only glycine among the amino acids has been so characterized in the laboratory. Finally, the determination of a molecular abundance from the observations is a complicated process because, for example, excitation conditions are typically far from thermodynamic equilibrium, inhomogeneities in density and temperature are normally present in the line of sight, and complicated radiative transfer effects occur (cf. Irvine and Hjalmarson, 1983).

Detailed descriptions of the molecular regions considered here are beyond the scope of this paper. Table 1, however, gives some physical parameters (see Irvine and Hjalmarson, 1983; Johansson et al., 1983). Briefly, Orion includes at least three distinct emission sources, and is an obvious site of ongoing massive star formation. What we refer to as the ridge is an extended region of high density near the center of the Orion cloud. The plateau, which is named for the shape of the spectral emission lines and not for any spatial structure, is a localized area characterized by high velocity gas flows, which perhaps originate in mass loss from a young star or stars. The hot core is a separate small, hot, and dense region which apparently contains an infrared source (protostar?). In contrast, the clouds TMC-1 and L134N are cold, dark condensations that are considerably closer to the solar system but much less

TABLE 1
Physical Characteristics of Source Regions

Region	Mass (Solar Masses)	Density (H_2/cm^3)	Temperature (K)
TMC-1/L134N	$10-10^2$	10^3-10^5	10 - 20
Orion ridge	10^2-10^3	10^4-10^6	50 - 100
Orion hot core	~ 10	10^7-10^9	100- 200
Orion plateau	3 - 30	10^6-10^7	90 - 150
IRC+10216	~ 1	10^3-10^{11}	10 - 1000

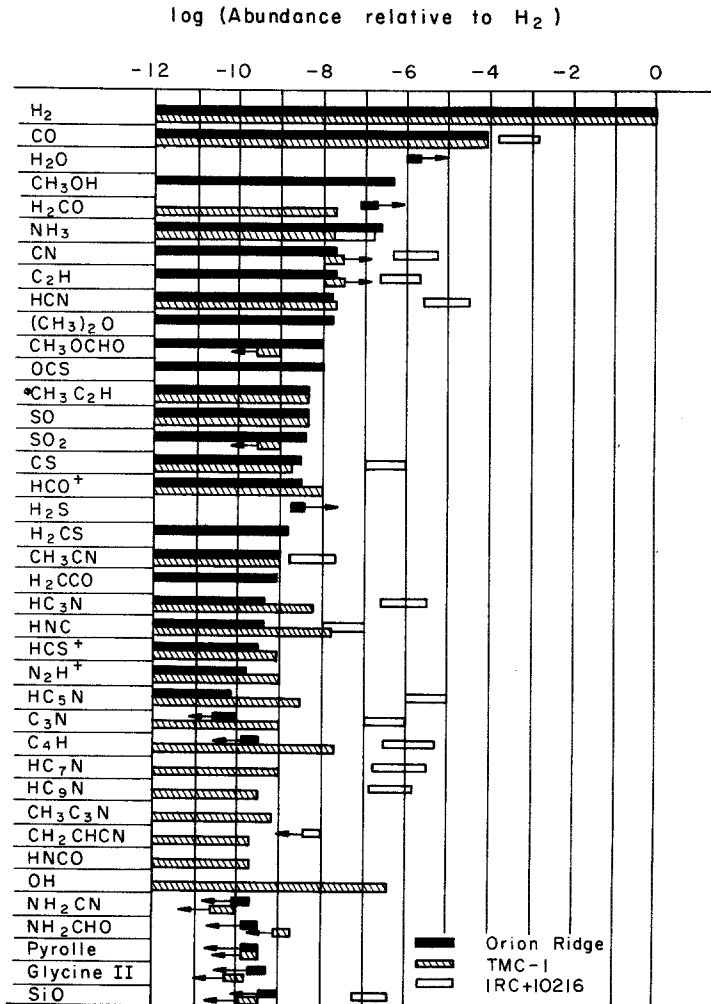


Figure 1. Abundances (number of molecules) for 3 regions.

massive overall than the Orion molecular cloud. It has been speculated that low mass, solar-type stars may form in these regions. Finally, IRC+10216 is an evolved star which has apparently undergone considerable nuclear processing in its interior and mixed some of the resulting products to the exterior, where they have been expelled to produce an extensive molecular envelope characterized by an elemental carbon to oxygen ratio >1 (the "cosmic" C/O ratio is 0.6). It is clear that substantial radial gradients in density, temperature, and perhaps certain molecular abundances exist in this envelope; our results represent some sort of radial average.

MOLECULAR ABUNDANCES

Molecular hydrogen is not observed directly in the regions considered here. However, observations of ultraviolet absorption lines in the spectra of background stars seen through low density regions, as well as observations of vibrationally excited infrared emission from hotter Orion gas, give very similar CO/H₂ ratios, and we have adopted the value $8 (10)^{-5}$ for both Orion and the dark clouds (Frerking et al; 1982; Watson, 1983). Note that all reported abundances will be molecular number density ratios relative to H₂. Other abundances are then determined by ratioing to observations of ¹³C¹⁶O or ¹²C¹⁸O, assuming a ¹²C/¹³C ratio of 40 in Orion and a terrestrial ¹⁶O/¹⁸O ratio. For the IRC+10216 stellar envelope the CO abundance is derived from an estimated mass loss rate (Johansson et al., 1983).

Because of uncertainties in the fractional CO abundance and other possible systematic and random errors, the quoted values in Figure 1 are probably not accurate to better than an order of magnitude. Abundance ratios, particularly for a single source, are much better determined, but even here uncertainties of a factor of a few may be present. Of course some individual ratios have been determined much more accurately (for example, HNC/HCN, to which we refer below). In Figure 1 a logarithmic scale is used, with a histogram presentation for the Orion ridge cloud and for TMC-1, while the width of the bar for the IRC+10216 values illustrates the uncertainty discussed above. Upper and lower limits for certain species are indicated by arrows. Several important features of the chemical composition are evident:

1. For most molecular species there is a surprising abundance uniformity over the range of temperature and density represented by the Orion ridge and TMC-1. In fact this general similarity extends to even lower densities, according to the observations of C₂H₃, HCN, HCO⁺, CS and CO for diffuse cloud material (density $\leq 10^3$ molecules per cm³) reported by Nyman (1983a, b). This is in strong contrast to some earlier studies which deduced a strong inverse dependence of abundance on cloud density for such species, and interpreted these results as evidence for depletion of gas phase

molecules onto the particulate grains in denser regions (Wooten *et al.*, 1980a, b). Apparently these previous results suffered from serious systematic errors resulting, at least in part, from an oversimplified treatment of radiative transfer (Stenholm, 1983). Why such depletion does not occur is an interesting unsolved question, but may involve cycling of material from the interior to the exterior of clouds, where evaporation and/or photodesorption take place (Boland and deJong, 1982).

2. More specifically, we note from Figure 1 that all observed molecular species are trace constituents relative to H_2 , as would be expected on grounds of cosmic abundance. The next most abundant observed species, CO, contains between 10 and 20% of the available carbon (some recent studies would make this value even higher; Scoville *et al.*, 1983). The depository of the remaining carbon is uncertain; in some cases an amount comparable to that in CO may be present as neutral atomic carbon (Phillips and Huggins, 1981), a substantial fraction may exist as graphite or amorphous carbon in the interstellar grains (Whittet, 1981), a poorly determined but presumably smaller amount may occur as simple hydrocarbons such as CH_4 and HCCH (e.g., Irvine and Hjalmarsen, 1983), and an also undetermined but possibly substantial fraction may be present as complex organic material coating the grains (Greenberg, 1983). The depository of nitrogen in these regions is also uncertain; although NH_3 is relatively abundant, in at least one interstellar cloud observations of N_2H^+ have been interpreted as showing that N_2 is as plentiful as NH_3 (Linke *et al.*, 1983). The abundance of such important oxygen-containing species as H_2O and O_2 is not well constrained by present observations, although observations of $^{16}O^{18}O$ in Orion indicate that O_2 is not more abundant than CO (unpublished observations at the Five College Radio Astronomy Observatory in the USA). The presence of radicals such as CN, C_2H , and OH provides ample evidence of the very nonequilibrium character of the chemistry in interstellar clouds.

3. In the sources considered here only upper limits are available on the abundance of several species of potential interest to chemical evolution, including NH_2CN (which has been used as a condensing agent in such experiments and has been detected in the Galactic center), all cyclic molecules such as pyridine and pyrrole, and amino acids such as glycine. Note, however, that the limits are not particularly low when compared to other molecules of comparable molecular weight. Thus, the failure to detect either cyclic species or molecules with branched heavy element backbones may be simply a matter of present instrumental sensitivity, rather than reflecting a basic characteristic of interstellar chemistry.

4. In spite of some general similarities, significant chemical variations do exist between TMC-1 and the Orion ambient (ridge) cloud: the abundances of acetylenic and polyacetylenic species are strongly enhanced in the former source, while NH_3 is relatively depleted. It is particularly interesting in this context that the cold cloud L134N (Table 1) is much more similar to Orion than to

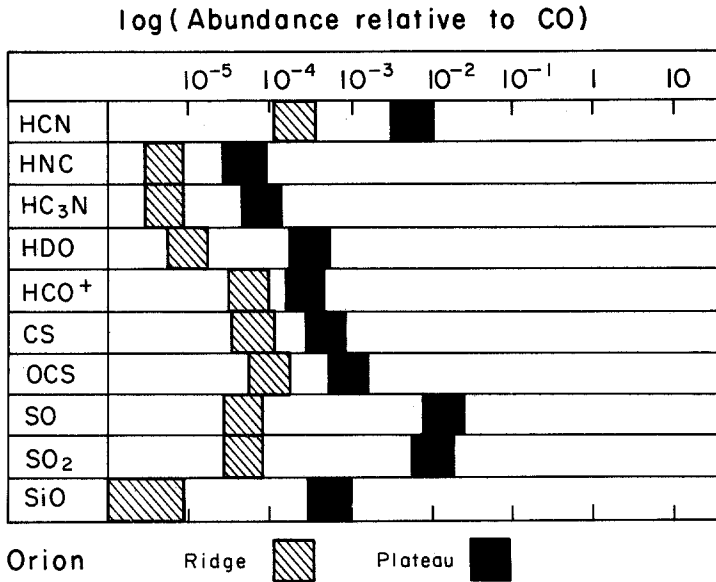


Figure 2. Abundances (number of molecules) for 2 regions in Orion.

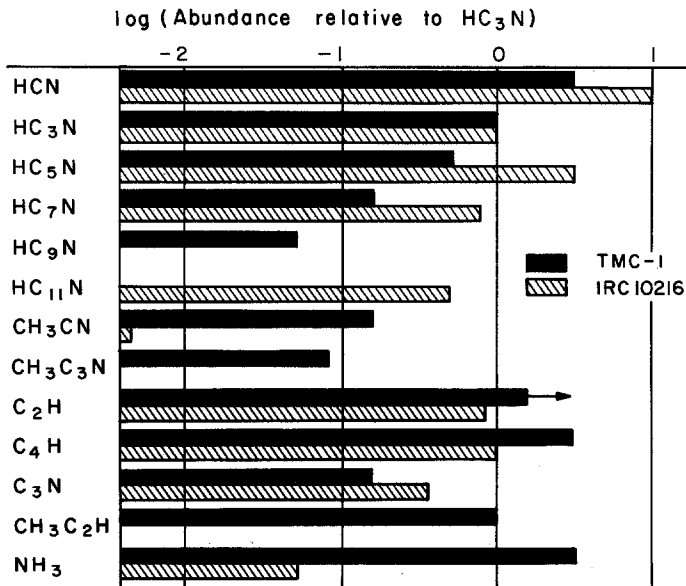


Figure 3. Abundances (number of molecules) for the dark cloud TMC-1 and the stellar envelope IRC+10216.

TMC-1 in these respects (Watson and Walmsley, 1983). Since the temperature and density are very similar for TMC-1 and L134N, this suggests that an additional factor may be acting to discriminate among these sources. It has been suggested that this may be cloud age (e.g., Hjalmarsen and Friberg, 1980), which raises the interesting possibility of tracing cloud evolution via observations of chemical composition. Alternatively, the differences may reflect the ultraviolet radiation field or differing elemental abundances (Freeman and Millar, 1983), possibly as a result of differential incorporation into the particulate grains.

5. The enhanced abundance of a number of molecules in the Orion plateau source relative to the extended ridge cloud is evident from Figure 2. These effects may be related to the previous thermal history of the gas in the plateau region, possibly as a result of shock heating or outflow from the envelope around an oxygen-rich star, either of which would enhance the importance of less exothermic reactions, as well as perhaps simply evaporating more volatile material from the grains (Watson and Walmsley, 1982). It may be noted in this connection that several species (CH_3OH , H_2CO , $(\text{CH}_3)_2\text{O}$, CH_3OCHO , OCS , SO , SO_2 , and HDO) appear to be enhanced in that part of the Orion ridge adjacent to the plateau source, possibly indicating "contamination" by material from the latter environment (Hjalmarsen and Irvine, 1983).

6. Figure 1 also shows that the abundances in the IRC+10216 circumstellar envelope are strikingly different from those in the more truly interstellar clouds. Both CO and HCN are enhanced in the case of IRC+10216, in agreement with thermal equilibrium calculations which predict that almost all oxygen and almost all nitrogen will be in these compounds (Lafont *et al.* 1982). Although the absolute abundance of a number of the acetylenic derivatives and nitriles is very much larger in IRC+10216 than TMC-1, the relative abundances (Figure 3) are strikingly different only in the case of CH_3CN .

7. The rather regular falloff in abundance of the cyanopolyynes in TMC-1 with increasing carbon chain length (Figure 3) has been interpreted as support for their production by Fischer-Tropsch type reactions (Hayatsu and Anders, 1981); in contrast, the observed deuterium fractionation of HC_3N and HC_5N has been cited as support for formation of the cyanopolyynes by gas phase ion-molecule reactions (Schloerb *et al.*, 1981).

8. Ratios of molecules with similar excitation requirements (collision cross section and electric dipole moment) can be obtained much more accurately than can the abundances relative to H_2 . Table 2 lists several such ratios, including a comparison of increasingly saturated members of the HC_3N series, and the isomeric pair HCN/HNC . It is seen that quite substantial differences exist among the source regions considered here. In the case of the HCN/HNC pair, the ratio in the IRC+10216 envelope is close to that expected under chemical equilibrium conditions in the stellar photosphere, suggesting that this result is "frozen in" as the envelope expands

TABLE 2
Abundance Ratios for Saturated/Unsaturated Nitriles and Isomers

	$\frac{\text{CH}_3\text{CH}_2\text{CN}}{\text{HC}_3\text{N}}$	$\frac{\text{CH}_2\text{CHCH}}{\text{HC}_3\text{N}}$	$\frac{\text{HCN}}{\text{HNC}}$
Orion Hot Core	7	1	?
Orion Ridge	≤ 1	?	50
TMC-1	≤ 0.2	0.03	1
IRC+10216	≤ 0.02	≤ 0.01	250

more rapidly than the chemistry can equilibrate (McGabe *et al.*, 1979). According to equilibrium calculations, virtually no HNC would exist in the lower temperature clouds; the actual results indicate the preeminent role of kinetics in the cold, low density interstellar medium (Goldsmith *et al.*, 1981). The varying degrees of chemical saturation among the observed sources in Table 2 has not previously drawn much comment. For the cold cloud TMC-1, the predominance of the unsaturated species may reflect the unreactivity of H_2 with small hydrocarbon ions in the gas phase (Herbst *et al.*, 1983; cf also Millar and Freeman, 1983). The situation in the Orion "hot core" presents an interesting contrast, the reasons for which are obscure; conceivably this is evidence for grain surface catalysis, which might result in high degrees of saturation (Watson, 1976).

In summary, quantitative molecular abundances in dense interstellar clouds and in circumstellar envelopes are now becoming available. Both similarities across a range of source conditions as well as interesting differences in the chemistry appear. As our understanding increases concerning the processes leading to particular compositions, we may hope to relate these findings to the evolution of molecular clouds and hence to the chemistry of regions where stellar and planetary formation are occurring.

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