Interstellar molecules

Radioastronomy reveals that clouds between the stars, once believed to consist of simple atoms, contain molecules as complex as seven atoms and may be the most massive objects in our Galaxy.

Philip M. Solomon

During the past three years, molecules have been discovered in interstellar clouds with an abundance and chemical complexity totally unexpected by astrophysicists. Twenty-three molecules in a total of 34 isotopic combinations have now been identified through radio spectral line observations at more than 75 wavelengths from 2 millimeters to 36 centimeters. An important new chapter in astronomy has begun, with potential already demonstrated for providing new information and insights into such basic problems as the cosmic abundance of isotopes, formation of stars, structure of the Galaxy and the Galactic nucleus, and the thermodynamics of the interstellar medium. Equally important, many completely new phenomena have revealed themselves as it becomes clear that the most massive objects in the Galaxy are molecular clouds (see figure 1), and the physics of these regions is only now being explored. In addition an entirely new field, interstellar chemistry, is developing now that we know that chemical evolution of matter into substances as complex as organic molecules has taken place throughout the Galaxy.

The molecules found to date in the interstellar medium range from simple diatomics to organic compounds with up to seven atoms. A complete list is given in Table 1. Of these, all except the first four (H_2, CH, CN and CH^+) were discovered at radio frequencies. Contributions to the growth of this field have been made by astronomers and physicists from about a dozen institutions. It is impossible in this brief discussion to review each discovery separately, and much of the fascinating work on maser radiation of H_2O and OH from stars and small compact sources, which are not truly interstellar, will not be covered. I shall emphasize the interpretation of data from massive molecular clouds in terms of the physical and chemical conditions in these regions and summarize some of our results of the past two years. The discussion will be based primarily on millimeter-wavelength observations with the 36-foot National Radio Astronomy Observatory (NRAO) antenna, Green Bank, West Virginia, carried out jointly with my colleagues Keith Jefferts, Arno Penzias and Robert W. Wilson, all of Bell Telephone Laboratories. The discussion will include sources of molecular line radiation, physical conditions in molecular clouds, Galactic structure (with the help of Nicholas Scoville), determination of isotopic abundances and interstellar chemistry. But before we can begin discussing these observations, we should look at some of the historical background.

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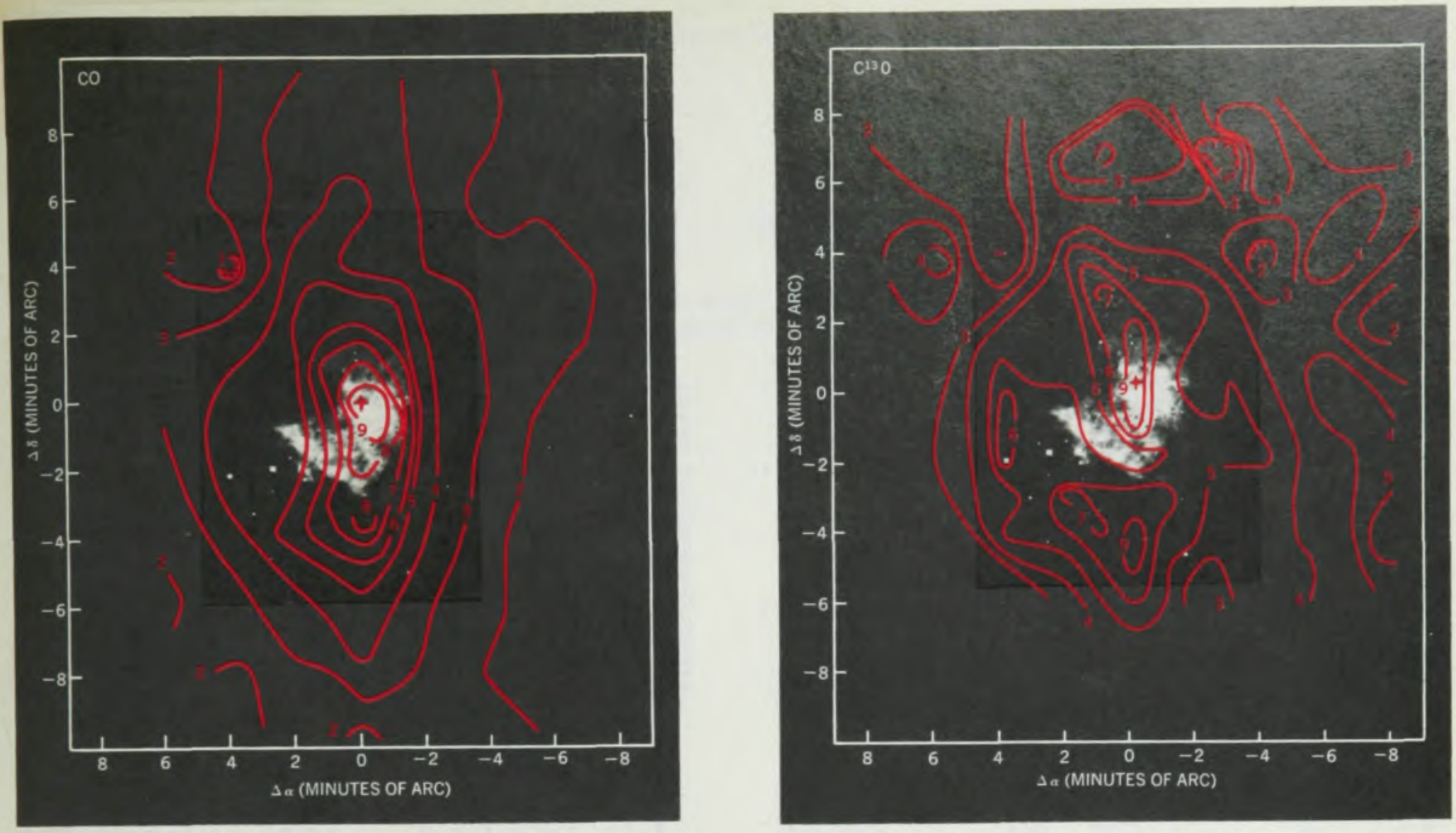
Early interstellar astronomy

Before molecular line astronomy, the interstellar medium was studied by optical astronomy, radio astronomy of atomic hydrogen at 21 cm and by continuum radio astronomy. These observations, combined with a large body of theoretical work, led to a model consisting of two basic components characterized by the ionization state of hydrogen as either HI (neutral hydrogen) or HII (ionized hydrogen, H^+). The average atomic-hydrogen density throughout the plane of the Galaxy was found to be one atom per cm^3, composed primarily of clouds with densities of about 10 to 50 atoms per cm^3 and of a much more tenuous intercloud medium.

The temperature of the HI clouds as measured by the 21-cm intensity is thought to be typically 50–125 K. The relative abundance of the elements is probably similar to solar abundance values: He/H is about 10^{-1}, O/H about 7×10^{-4}, C/H about 3×10^{-4} and N/H about 1×10^{-4}, with all other elements less than 10^{-4}. The existence of Ch, CH^+ and CN as well as of atomic Ca, Ca^+, Na, Fe, Ti^+ and K in the interstellar medium has been known for almost 40 years from the appearance of narrow interstellar absorp-



CO and $C^{13}O$ emission intensity in Orion A molecular cloud. Placing these contour maps over photo of optical emission nebulae from the foreground HII region shows peak CO emission centered on a strong infrared point source and an extended source, all within the central 1/2 arc min, along with OH maser sources. Total cloud size is at least 30 light years and total mass about 10^5 solar masses. Coordinates are centered at $\alpha = 5^h32^m47^s \pm 1^s$, $\delta = -5°24'20'' \pm 15''$; 10 contour units = 200 K km/sec for CO; 30 for $C^{13}O$. Ori B, W51, DR21 and Sgr B are similar, as are many clouds not linked with HII. Figure 1

tion lines superimposed on the optical spectra of bright stars. Although the atomic lines are much stronger, molecular interstellar optical lines are observable in a large number of stellar spectra. A survey conducted at Mt Wilson by Walter Adams[1] in 1949 found CH^+ interstellar lines in 70 out of 300 stars, with CH, CN, or both present in about 30 cases. These absorption lines at roughly 4000 Å were formed by transitions from the ground electronic state to excited electronic states that happen to occur at the wavelengths transmitted through the optical atmospheric "window."

The hydrogen in HII regions is photoionized by ultraviolet radiation from hot stars (T about 20 000 K), so that a high degree of ionization is maintained around the star. The transition boundary between HII and HI regions is sharply defined at a radius where the recombination of protons and electrons competes with the photoionization to produce sufficient neutral hydrogen for absorbing all remaining ionizing photons. The HII regions are heated by the ejected photoelectrons and typically have temperatures of about 10 000 K. HII regions, particularly the Orion Nebula, which is the brightest and one of the nearest to the Sun, have been extensively studied by optical observation of emission—continuum and line.

The low density and exposure to strong photodissociating radiation made it seem unlikely that molecules of any complexity could exist in either HI or HII regions. What was overlooked in this picture was the importance of entire regions that simply did not radiate at optical frequencies, did not show up clearly at 21 cm and were therefore largely ignored.

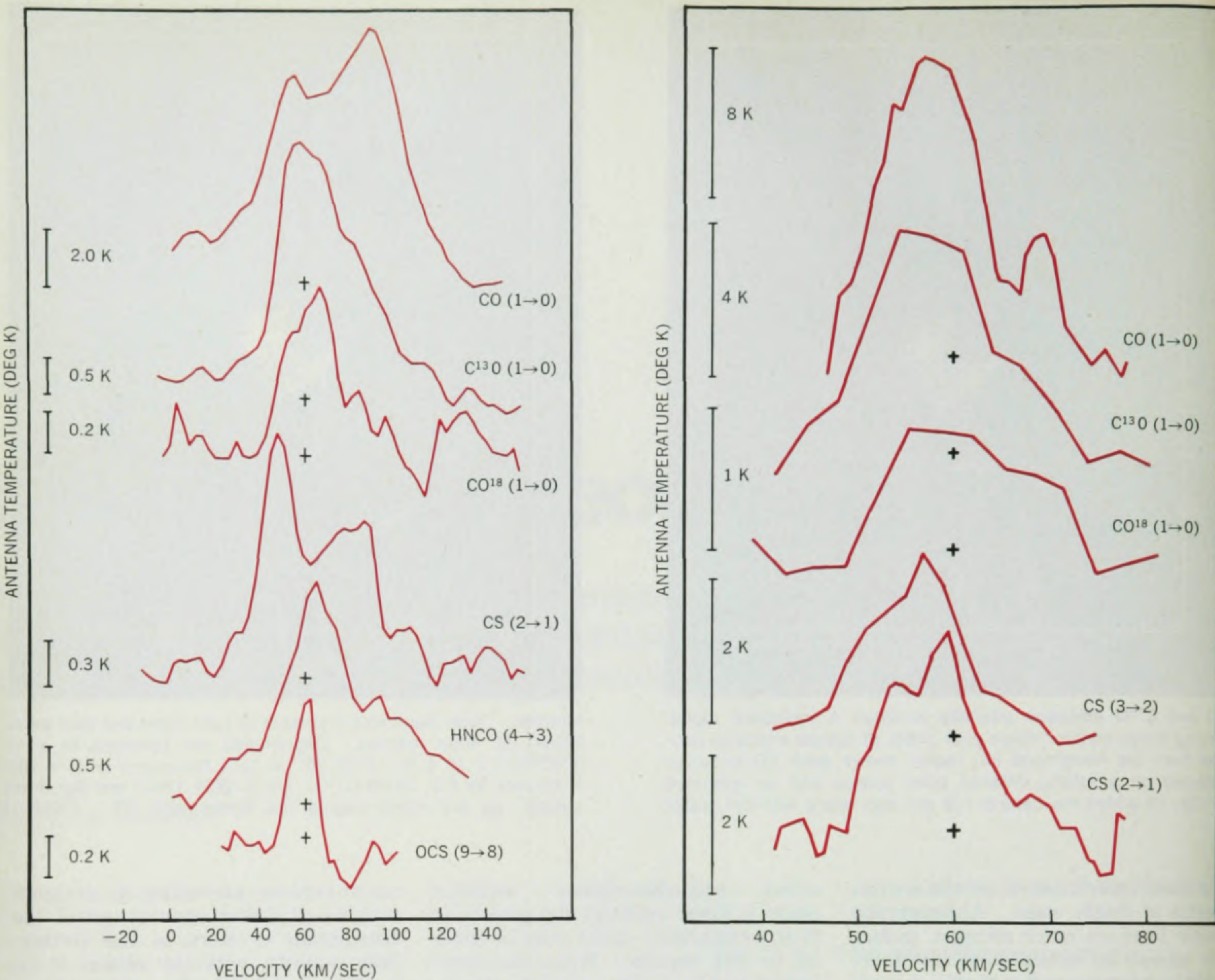
Another major constituent of the interstellar medium that became generally recognized in the mid 1920's is interstellar dust. Dust particles are mixed in with the gas and contain about one percent of the mass in interstellar space. These small solid particles, primarily silicates, of submicron size (about 0.2 microns) absorb and scatter light, which prevents stars from being observable in the plane of our Galaxy over distances much greater than 3000 light years (1000 parsecs). A glance at the Milky Way on a moonless night reveals the dark lanes that are regions of strong dust concentration, relatively near to the Sun. The optical scattering by the dust has a wavelength dependence of λ^{-1}, and is usually referred to as "interstellar reddening."

From the point of view of optical stellar astronomy, these dusty regions of dark clouds, whose presence and number has been amply demonstrated in optical photographs by Bart Bok, have usually been regarded as a curious annoyance preventing an accurate analysis of stellar spectra and of the distribution of stars in the Galaxy. Only recently, with the advent of infrared and molecular line observations, has any substantial progress been made in studying these regions.

Early molecular studies

Molecular radio astronomy began in 1963 with the discovery[2] of the Λ doubling transition from the OH radical at 18 cm by a group at the Massachusetts Institute of Technology and the Lincoln Laboratory. Following this discovery was a burst of activity in OH observations, which led to the detection of maser radiation, thermal emission lines and absorption lines observed against the background of radio continuum radiation from HII regions and other strong sources. Although the OH observations showed a fascinating variety of phenomena, the estimated relative abundance OH/H was very low. A remarkable list[3] of candidate molecules, with frequencies determined from microwave spectroscopy, including NH_3, H_2O and CO in addition to OH, had been suggested by Charles Townes in 1955. However, the view that interstellar clouds were composed primarily of atoms with a small mixture of simple radicals still prevailed.

Five years later, a group at Berkeley



Millimeter spectral lines observed for several molecular transitions in direction of SgrB (left) and W51 clouds. Intensity (expressed as T_a) is shown as a function of velocity relative to the mean motion of stars near the Sun. Crosses are at 60 km per sec and zero T_a for each line. Spectra for W51 are from reference 10 (1973). Figure 2

searched for and discovered ammonia[4] (NH_3) and water at 1.26 and 1.35 cm. The H_2O line was observed as a strong maser with intense emission from numerous small regions including infrared stars, and the NH_3 was found in two extended clouds near the Galactic center. At about the same time as these microwave discoveries of new molecules, Carl Heiles's[5] observations of thermal OH emission in dark clouds with little or no 21-cm radiation led to the first strong evidence that entire clouds might be dominated by molecular instead of atomic hydrogen. Theoretical arguments[6] on the formation and dissociation of molecular hydrogen showed that hydrogen molecules formed on grain surfaces in dense clouds (total hydrogen density greater than 100 cm^{-3}) would be self-shielded against photodissociation, producing entire clouds whose hydrogen is almost entirely in molecular form. However, H_2 is a symmetric molecule with no permanent electric dipole moment and therefore has only extremely weak rotational transitions, none of which fall in the radio range, so that the evidence for H_2 remained indirect until the later rocket ultraviolet detection of the Lyman absorption band.

A search for new interstellar molecules, carried out at NRAO completely independently of the Berkeley group, was based on the realization that the organic molecule formaldehyde (H_2CO) was a good candidate for detection through a transition at 6 cm, due to k-type doubling of the lowest orthoformaldehyde rotational state (J = 1). Absorption at 6 cm by formaldehyde was discovered by Lewis E. Snyder and his coworkers[7] in the well known sources Sgr B and Sgr A, near the Galactic center. The absorption was observed in the direction of the strongest HII regions in the Galactic plane as well as in dark clouds with no continuum source in the background.

The widespread observability of H_2CO, whose abundance is about 10^{-8} times that of hydrogen, is due to the refrigeration of the k doublet by a nonequilibrium process resulting in an excitation temperature below that of the Penzias–Wilson microwave background[8] (brightness temperature T_b equal to 2.8 K). The presence of an organic molecule in clouds, near HII regions as well as in numerous dark clouds, clearly indicated that the chemical complexity of the interstellar medium was greater than anyone expected, although only small fractions of any element had been observed in molecular form.

A third area of investigation was the observation of molecules through their millimeter rotational lines. Although the technology involved was still in an earlier stage of development, it presented the opportunity to select molecules on the basis of astrophysical interest. As a result of discussion between Penzias and me on the best candidate molecules, the Bell Labs group searched for and found emission from

Table 1. Molecules Observed in the Interstellar Medium

Molecule	Frequency of discovery line (GHz)	Discovery transition	Isotopic species observed	Number of different radio transitions observed in all isotopic species	Approximate density* in molecular clouds (cm^{-3})
H_2	No radio lines; ultraviolet only in tenuous clouds; abundance in dense clouds deduced from CO observation and excitation				10^{+4}
CH^+	Optical only	—	$C^{13}H^+$	—	Not observed in H_2 clouds
CH	Optical only	—	—	—	Not observed in H_2 clouds
CN	Optical and 113.492	$J = 1 \rightarrow 0$	—	1	10^{-4}
OH	1.665	$J = 3/2$ Λ doubling	$O^{18}H$	10	10^{-2}
CO	115.271	$J = 1 \rightarrow 0$	$C^{13}O$; CO^{18}	3	1
CS	146.969	$J = 3 \rightarrow 2$	CS^{34}; $C^{13}S$	7	10^{-3}
SiO	130.268	$J = 3 \rightarrow 2$	—	1	(10^{-5})
H_2O	22.235	$J_{K_{-1}K_1} = 6_{16} \rightarrow 5_{23}$	—	1	? maser only
HCN	86.339	$J = 1 \rightarrow 0$	$HC^{13}N$; HCN^{15} DCN	6	10^{-3}
H_2S	168.762	$J_{K_{-1}K_1} = 1_{10} \rightarrow 1_{01}$	—	1	10^{-4}
OCS	109.463	$J = 9 \rightarrow 8$	—	4	(10^{-4})
NH_3	23.694	$J_K = 1_1$ Inversion doublet	—	7	10^{-2}
H_2CO	4.830	$J_{K_{-1}K_1} = 1_{11} \rightarrow 1_{10}$	$H_2C^{13}O$; H_2CO^{18}	10	10^{-4}
H_2CS	3.139	$J_{K_{-1}K_1} = 2_{12} \rightarrow 2_{11}$	—	1	10^{-5}
HNCO	87.925	$J_{K_{-1}K_1} = 4_{04} \rightarrow 3_{03}$	—	3	(10^{-4})
HCOOH	1.639 (possible)	$J_{K_{-1}K_1} = 1_{01} \rightarrow 1_{11}$	—	1	—
HC_3N	9.098	$J = 1 \rightarrow 0$	—	3	(10^{-4})
CH_3OH	0.834	$J_{K_{-1}K_1} = 1_{11} \rightarrow 1_{10}$	—	9	10^{-3}
CH_3CN	110.383	$J_K = 6 \rightarrow 5$	—	5	(10^{-4})
NH_2HCO	4.619	$J_{K_{-1}K_1} = 2_{11} \rightarrow 2_{12}$	—	1	(>10^{-5})
CH_3C_2H	85.457	$J_K = 5_0 \rightarrow 4_0$	—	1	(10^{-4})
CH_3HCO	1.065	$J_{K_{-1}K_1} = 1_{10} \rightarrow 1_{11}$	—	1	(>10^{-5})

**The densities are normalized to a typical molecular cloud with a hydrogen density of 10^4 cm^{-3}; values are arrived at from published column densities and estimates of optical depth effects; brackets indicate molecules observed only in Sgr B or A, near the Galactic center.*

carbon monoxide at 2.6 mm. As soon as the receiver was turned on, with a one-second time constant, Wilson noticed a strong emission line from the direction of the Orion Nebula. This initial discovery[9] and subsequent joint observations[10] by Jefferts, Penzias, Wilson and me have shown that carbon monoxide is more abundant by a factor of 10^3 than any other molecule (except H_2) and is observable throughout the plane of the Galaxy over a wide range of velocities, in virtually all dark clouds[11] as well as near HII regions. The ubiquity of carbon monoxide and the relative simplicity of the energy levels make observations of CO and its isotopes $C^{13}O$ and CO^{18} particularly useful for studying the physical conditions and kinematics of interstellar clouds.

Millimeter-wave astronomy

Following this discovery in 1970, there was very rapid progress in observations of interstellar molecules, primarily although not solely at millimeter wavelengths. This progress is due in large part to the development of receivers for millimeter-wave observations, principally by Bell Labs in conjunction with NRAO. The importance of millimeter waves, as opposed to the more conventional centimeter and meter wavelength radio astronomy, arises primarily because the fundamental rotational transition frequency, which is inversely proportional to the reduced mass, is in the range 50–150 GHz (wavelength 6 mm–2 mm) for diatomic molecules composed of the cosmically abundant heavy atoms C, N, O and S. For simple polyatomic molecules that may include hydrogen and three or four of the others (OCS, HNCO), the lowest-frequency *rotational* transition is typically 10–50 GHz (3.0 cm–6 mm) but there are a large number of rotational transitions between low-lying excited states (such as $J = 9 \rightarrow 8$ in OCS) that also fall in the range 50–150 GHz. The splitting of a rotational level may cause some molecules to have longer-wavelength transitions, but virtually all molecules with an electric dipole moment and at least two heavy atoms have millimeter rotational lines that can be observed from the ground.

Another important advantage of short wavelengths is the high spatial resolution available even with moderate-size single antennas. The NRAO 36-foot antenna for millimeter waves has a 1.1 arc-min beam size at the CO 2.64-mm line, which is ten times higher resolution than can be achieved at 21 cm by the world's largest steerable antenna. This dish at NRAO has been used for all of the millimeter-wave discoveries; those made by outside groups as well as those discoveries made by Observatory staff.

Molecular clouds

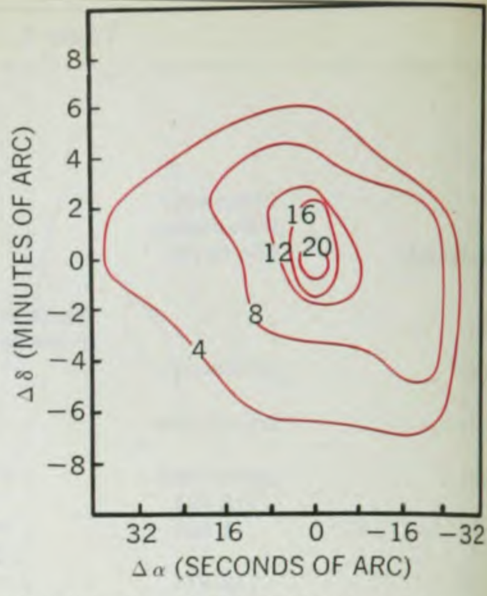
The two most frequently observed sources for interstellar molecules are molecular clouds associated with the

HII regions Ori A and Sgr B. Sgr B and dozens of other HII regions distributed throughout the Galactic plane were discovered by continuum radio astronomy from thermal bremsstrahlung emitted by the hot gas. These regions represent a class of dense ionized clouds surrounding hot stars, frequently hidden by interstellar dust. Samples of spectra from Sgr B (distance about 30 000 light years) and W51 (about 20 000 light years) are seen in figure 2. All molecules in Table 1 have been found in Sgr B and some of the more complex ones have been detected only there. This is the richest molecular cloud in the Galaxy and is part of a large complex of clouds in the Galactic center region. I have chosen these regions for sample spectra because of the substantial velocity structure they show, particularly in CO, indicating the presence of molecules along the line of sight with a wide range of radial velocities. CO emission ($J = 1 \rightarrow 0$) is observed from clouds associated with dozens of HII regions, the strongest lines originating from Ori A, M17, Ori B, W51 and DR 21. Millimeter rotational-emission lines from several other molecules such as CS and HCN are also seen from many HII region clouds but always at lower intensity than either CO or $C^{13}O$ emission.

Mapping of these molecular clouds shows extended sources usually but not always peaking near the center of the HII region. These sources have small condensations detected by their OH and H_2O maser radiation with the maser position usually very near the strongest CO position. In addition, infrared radiation at 10–20 microns and at 100 microns has been found for most HII regions. The largest structure, however, is observed in carbon monoxide, frequently extending out to more than 30 arc-min from the center. The velocity of peak CO or CS emission indicates a cloud moving relative to the HII regions at about 1 to 10 kilometers per sec.

The prototype region for observing structure is the Ori A cloud, which is only 1500 light years from the Sun and has the added benefit of an observable optical-emission region long recognized as one of the youngest objects in the Galaxy, as well as a site of recent star formation; Harvey Liszt has been a contributor to the observations and to the mapping of Orion that form the basis of our discussion here. Figure 1 shows detailed contour maps of integrated intensity in CO and $C^{13}O$ emission centered on the position of the infrared and OH sources. Optical photographs show that the visible region is smaller than the molecular cloud, which is hidden behind the HII region. The extent of the Orion cloud has also been mapped in millimeter emission lines of CS, H_2CO, HCN and CH_3OH by several groups.[12-15] The distance between half-power points decreases from four arc-min by nine arc-min for CO and slightly less for CS ($J = 2 \rightarrow 1$) to less than two arc-min by two arc-min for lines from excited states of methyl alcohol.

Dark clouds are another important class of sources; these are simply dense molecular clouds not associated with HII regions. These sources all show carbon monoxide emission of varying intensity, frequently spread over areas greater than two arc deg in extent. Mapping of these clouds is only beginning, but structure indicating centers of intense emission is already indicated, and very strong sources, as yet unobserved, may very well exist in the dark clouds.



Contour map of the total column density in $C^{13}O$ centered on Sgr B2 (OH), with velocity between 50 and 75 km per sec. An intensity map for the optically thick $C^{12}O$ line would cover over 30 times this area. The distance of Sgr B from the Sun is about 30 000 light years, and 1 arc min is about six light years. Figure 3

Density, temperature and mass

One of the most important applications of molecular line astronomy has been as a diagnostic tool for analyzing physical conditions such as temperature, density, mass and internal motion of the interstellar clouds. The observations may be related to the physical properties of the clouds by considering the equation of radiative transfer and the collisional and radiative processes responsible for the excitation of the molecules. Consider the emission received from a transition between a lower level m and an upper level n where T_{nm} is the Boltzmann excitation temperature describing the population of the two levels. The measured intensity I of the emission line from the cloud is then given by the radiative transfer equation

$$I_\nu = B_\nu(T_{mn})(1 - e^{-\tau_\nu}) \qquad (1)$$

where B_ν (T) is the Planck function and $\tau_\nu = N_m \alpha_\nu$ is the optical depth through the cloud of the line at a frequency ν. N_m is the column density in cm^{-2} through the cloud, and α_ν is the absorption coefficient.

For a source with angular size large compared to the antenna beam, $I(\nu)$ can be determined directly from the measured total power received at the antenna. All measurements are obtained relative to the microwave background, which, although weak, must be accounted for in determining $I(\nu)$.

As can be seen from equation 1, for the optically thick case ($\tau \gg 1$), the intensity is a measure of the state temperature T_{mn}, whereas for the optically thin case ($\tau \ll 1$), the intensity is proportional to the column density of molecules N_m. For $h\nu \ll kT$, equation 1 can be written in terms of the brightness temperature T_b

$$T_b = T_{mn}(1 - e^{-\tau_\nu})$$

which gives, for $\tau_\nu \gg 1$

$$T_b = T_{mn} \qquad (2)$$

and (substituting $\tau_\nu = N_m \alpha_\nu$) for $\tau \ll 1$

$$T_b(\nu) = N_m \alpha_\nu T_{mn} \qquad (3)$$

Thus for $\tau \gg 1$, the observed brightness temperature is independent of the column density and is simply equal to the state temperature.

The molecular abundance in the form of the column density can be determined from the optically thin case and a knowledge of the absorption coefficient. The frequency dependence of α_ν is a function of the radial-velocity distribution of molecules along the line of sight. It is therefore useful to use the integrated absorption coefficient $\alpha = \int \alpha_\nu d\sigma$. With $|\mu|_{mn}$ as the dipole-moment matrix element, we find

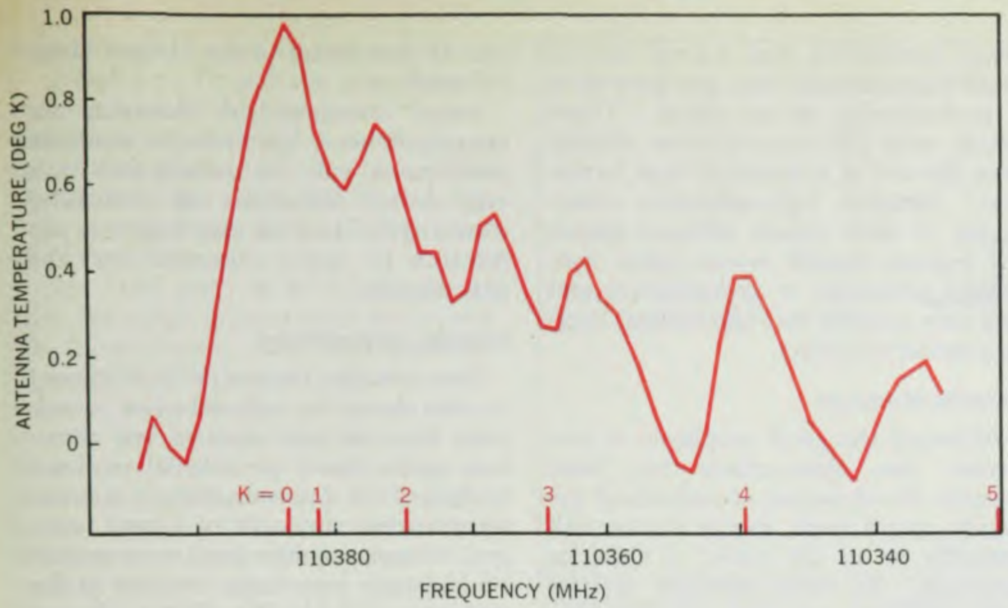
$$\alpha = \frac{8\pi^3}{3hc}|\mu_{mn}|^2 \nu[1 - \exp(-h\nu/kT_{mn})] \qquad (4)$$

The term in brackets, due to stimulated emission, is proportional to the excess of molecules in the lower state m relative to the upper state n. For $h\nu \ll kT_{mn}$, the abundance can be determined independently of the state temperature from equations 3 and 4, and is given by

$$N_m = \frac{3k}{8\pi^3|\mu_{mn}|^2\nu}\int T_b dv \qquad (5)$$

where the intensity is integrated over velocity (in kilometers per sec). Thus, both state temperature and abundance can be determined from observation of intensity, but not from the same spectral line.

Typical brightness temperature T_b of observed millimeter emission lines are in the range of 4 K, just above the background radiation, for the weakest



Methyl cyanide emission from Sgr B2 (OH) in the $J = 6_K \rightarrow 5_K$ transition. Five lines, from K = 0–4, contribute to the profile. Relative intensities of the lines indicate a Boltzmann temperature of about 150 K for the K-level population. The K levels do not mix radiatively, so this temperature indicates the kinetic temperature. Observations only 1 arc min from this position show much lower excitation temperatures. Figure 4

detectable lines to 45 K for the core of the Orion Nebula molecular cloud in the carbon monoxide transition at 2.6 mm. Equation 5 may be applied in a straightforward manner with observed brightness temperatures to obtain lower limits to true column densities N_m on the assumption that τ is less than one. These values of N_m must be multiplied by an estimated ratio of the total number of molecules divided by the fraction in state m, N/N_m. N is typically in the range 3×10^{12} to 3×10^{16} cm^{-2}. Any molecule producing an optically thin line is clearly a very minor constituent of the cloud since molecular hydrogen column densities are expected to be much greater than 10^{21} for optically opaque clouds.

To understand the physics of these clouds and their relation to the formation of star clusters, the most important quantities that must be obtained are the hydrogen density, which gives the total mass, and the kinetic temperature. We have used two methods to estimate the mass of molecular clouds. The first, which gives a lower limit, is application of equation 5 to the column density of $C^{13}O$, which is then scaled to the hydrogen density by employing observed isotope ratios $C^{12}O/C^{13}O$ and the cosmic abundance H/C. (We shall discuss isotope ratios later on.) The column density of $C^{12}O$ cannot be directly measured, because the optical depth is much greater than one. From equation 5, substituting for $C^{13}O$ ($J = 1 \rightarrow 0$) the total column density in all states is

$$N_{C^{13}O} = 5 \times 10^{13} T_{01} \int T_b dv \qquad (6)$$

In obtaining equation 6 the $\Sigma(N_i/N_0)$ ratio has been approximated by the rotational partition function and by assuming a Boltzmann distribution at T_{01}. The state temperature T_{01} comes from $C^{12}O$ observations and equation 2, with the assumption that T_{01} is the same for both isotopic species. A map of the abundance of $C^{13}O$ in Sgr B is seen in figure 3.

Observations of isotope ratios in many clouds indicate that $C^{12}O/C^{13}O$ is about 89, similar to the terrestrial value; therefore N_{CO} is about equal to 89 $N_{C^{13}O}$. The C/H cosmic abundance is 3×10^{-4}. For a cloud of size l, assuming all the carbon is in the form of CO, we find that

$$N_{H_2} = n_{H_2} l \geq 1.4 \times 10^5 N_{C^{13}O} \qquad (7)$$

is a *lower limit* to the total hydrogen column density.

Mechanisms of excitation

A second way to estimate the hydrogen density is to consider the processes determining the excitation temperature T_{mn}. The population of levels and therefore the excitation temperatures in an interstellar cloud are determined by collisions and by interaction with radiation. We can show from theoretical considerations and comparison with observation that the most important source of excitation, particularly for CO, is collisions with H_2.

If collisions completely dominate the exchange of population between states, then all state temperatures would equal the kinetic temperature of the gas. In this case all lines with τ much greater than one would have the same intensity. However, emission lines observed in many sources[12] from CS ($J = 3 \rightarrow 2$) at 147 GHz and CS ($J = 2 \rightarrow 1$) at 98 GHz are always of much lower intensity (T_b = 9 K in Orion) than emission from either CO (T_b = 45 K in Orion) or even $C^{13}O$ (T_b = 13K in Orion). Although this could conceivably be due to low optical depth in CS, observations of very extended emission from CS as well as from the isotopic CS^{34} indicates a high optical depth, with τ much greater than one for CS. We therefore conclude that the state temperatures are lower for CS than for CO.

An important difference between the two molecules is the dipole moment and consequently the spontaneous decay rate A_{nm}, which is proportional to $|\mu_{mn}|^2\nu^3$. For CO, with a permanent dipole moment of only 0.1 debye, A_{10} equals 6×10^{-8} sec^{-1}; for CS with a permanent dipole moment of 2.0 debye, A_{32} is 6.5×10^{-5} and A_{21} is 1.8×10^{-5} sec^{-1}. Electron collision rates, unlike those for neutral particles, also scale with the transition strength $|\mu_{mn}|^2$.

Therefore the ratio $n_e\sigma v/A_{nm}$ of excitation upward by electron collision to de-excitation $n \rightarrow m$ by radiative decay will be independent of the dipole moment $|\mu_{mn}|$, so that population ratios n_n/n_m and temperatures T_{mn} that are independent of the transition strength will result for electron excitation. But observation of low temperatures for all strong dipole moment transitions (short lifetime) rules out electrons as responsible for the excitation.

The high CO and low CS brightness temperatures can be readily understood if excitation is by neutral particles, the most abundant being H_2. The collisional cross-section σ for this process, only weakly dependent on transition strength, is about 10^{-15} cm^2, so that the excitation rate $n_{H_2}\sigma v$ is about equal to $5 \times 10^{-11} n_{H_2}$ sec^{-1}, where n_{H_2} is the number density per cm^3 of hydrogen molecules. For a two-level system the minimum density required to bring the excitation temperature up to the gas kinetic temperature T is

$$n_{H_2} > \frac{A_{nm} kT}{\langle \sigma v \rangle h\nu_{nm}} \qquad (8)$$

For a transition at about two to three millimeters, $h\nu/k$ is about 5 K and we have n_{H_2} greater than or equal to 4×10^{10} $A_{nm}T$, which yields n_H greater than or equal to 10^4 for CO at 50 K. The required density for CS ($J = 3 \rightarrow 2$) to heat up to 50 K is n_{H_2} greater than 10^7 cm^{-3}. This two-level analysis has ignored the complications of multiple quantum collisions ($\Delta J > 1$) which can yield a very high nonthermal excitation temperature at low density, even for a simple rotational ladder; however, this effect is only important for an optically thin gas and will not produce high intensities at low collision rates.

Since CO emission is seen extensively near HII regions as well as near dark clouds at brightness temperatures from 5 K to 45 K, we can conclude that in general *the density of molecular hydrogen in large molecular clouds is in the range* 10^3–10^4 cm^{-3}. (This is 100 times greater than in atomic clouds.) There are undoubtedly small condensed objects, as in the core of the Orion Cloud, with n_{H_2} greater than or equal to 10^7 cm^{-3}. The subthermal excitation of CS and other short-lifetime transitions probably involves a combination of collisions and radiative trapping of line photons from condensed molecular cores.

The mass of the molecular clouds can then be estimated from either of the methods above (equation 7 or 8), because the scale size is determined from mapping and a knowledge of the distance, which is at least *approximately* known for most sources. The size l is greater than ten light years for the Orion Cloud and as large as 50 or 100 light years for the complex clouds near the Galactic center. Masses, determined for at least a half dozen clouds,[10] are in the range of 10^4–10^5 solar masses (one solar mass is 2×10^{33} gms). Molecular clouds are therefore among the most massive objects in the Galaxy, dwarfing the HII regions associated with many of them. The well known dark cloud complexes near the Sun (in the constellations of Taurus and Ophiuchus) are examples of massive molecular regions not associated with HII regions. The total number of these clouds in the Galaxy cannot yet be estimated, because only those near HII regions have so far been mapped. However, preliminary observations throughout the plane of the Galaxy indicate that a rather substantial fraction of the total mass in the Galactic plane may be in molecular clouds.

For regions where the density of hydrogen is greater than that given by equation 8, the CO state temperature will come into equilibrium with the kinetic temperature, and the measured brightness temperature will equal the kinetic temperature.[11] The kinetic temperature ranges from a low of about 6 K in the coldest areas to a high of about 45 K. Temperatures as high as 150 K are deduced from the excitation of highly excited lines[15,16] of complex molecules, but these apply only to small central cores associated with infrared objects. In figure 4, for example, we see the spectrum of methyl cyanide obtained from the center of the Sgr B cloud.

These clouds of high mass and low temperature are unstable to gravitational contraction, and a great deal of cloud fragmentation and star formation is undoubtedly taking place. Those clouds with HII regions have already been the site of substantial star formation. Detailed high-resolution observation of dark clouds without known HII regions should reveal many condensed protostars or protoclusters and give new insights into the earliest stages of stellar evolution.

Galactic structure

Although the great emphasis of molecular line observations has been towards the structure of individual gas clouds, much work in the future will probably be in the realm of Galactic structure. As radio receivers become more sensitive, we may map the molecular lines not only in the central densest regions of the clouds but also across the tenuous bridges that may connect one cloud to its neighbors. Measurements at 21 cm of atomic hydrogen have been very useful in analyzing the kinematics of the Galaxy. However, the most interesting Galactic structure phenomena may show themselves in regions where the gas has been compressed to the point where molecular hydrogen is dominant. Thus many of the strongest H_2CO and CO lines, particularly near the Galactic center, occur at Doppler velocities with only very weak 21-cm emission. In the Galactic-center region, where the relative abundance of molecules appears exceptionally high, interesting dynamical phenomena are being observed for the first time via molecular transitions.

Surveys of OH and H_2CO absorption[17,18] and CO emission[19] in the plane of the Galaxy at Galactic longitudes 358 deg–5 deg show molecular clouds plentiful over the entire region. Velocities are observed in CO (with respect to the mean velocity of stars in the solar neighborhood) from -250 to $+250$ kilometers per sec. CO emission is observed from both sides of the Galactic center, whereas absorption in H_2CO and OH shows up mainly in clouds on the solar side of the Galaxy in front of most of the continuum radiation.

The large-scale radial velocities observed cannot be interpreted in terms of Galactic rotation. Figure 5 is a schematic representation of a ring of clouds surrounding the center of the Galaxy at a distance of about 1000 light years. This ring contains the clouds near Sgr B and Sgr A as well as many other massive regions. The entire structure is expanding outward from the center of the Galaxy at about 100 kilometers per sec, with a total mass of at least 10^7 solar masses, and a kinetic energy in excess of 10^{54} ergs. This is probably a result of an explosion in the center of the Galaxy about 10^6 years ago.

Large antennas are desirable for many problems, but Galactic structure phenomena can be investigated with very small telescopes at millimeter wavelengths, and we may expect active research by many observers over the next decade.

Isotopic abundances

The isotopic frequency shift caused by the change in reduced mass is very large for rotational spectra and therefore radio lines provide a powerful technique for determination of isotopic abundances. Isotopes of carbon, oxygen, nitrogen, sulfur and, most recently, hydrogen have been detected in the molecules CO, H_2CO, HCN, CS and H_2S. The most extensively observed isotopic lines are of $C^{13}O$ and CO^{18}. For determination of abundances to be possible the lines must of course be optically thin. For this reason direct comparison with saturated lines from CO or CS can be misleading.

However, lines from the rarer isotopes C^{13} or O^{18} apparently are in general optically thin, and abundance should then be proportional to observed integrated intensities; that is, $\int T_A \, dv$ approximately equals $T_A \, \Delta v$. We have recently surveyed $C^{13}O$ and CO^{18} in about nine sources;[21] the data strongly indicate that both C^{13}/C^{12} and O^{18}/O^{16} are within a factor of two of their terrestrial values, since the observed ratios of

$$\frac{\int T_A dv(C^{13}O)}{\int T_A dv(CO^{18})} = 5\text{–}10$$

which is very close to that expected for terrestrial values;

$$\frac{C^{13}O}{CO^{18}} = \frac{499}{89} = 5.5$$

This implies that the material in the molecular clouds has had a nuclear history not substantially different from terrestrial matter. In particular, the molecular cloud material has not been through the carbon cycle in stellar interiors.

Similar results indicating approximately terrestrial ratios of N^{15}/N^{14} have been obtained for the Orion Cloud[22] from observation of HCN ($J = 2 \rightarrow 1$). CS[34] has also been extensively observed but $C^{13}S$ is seen only weakly in the Orion Cloud. Therefore, accurate sulfur isotopic abundances have not yet been determined. There are also optical results[23] from CH^+ lines that indicate terrestrial carbon abundance in a completely different type of interstellar cloud.

The first great surprise in isotopic observations is the abundance of deuterated hydrocyanic acid DCN in the Orion Cloud.[24] This molecule has been observed in two transitions, $J = 2 \rightarrow 1$ and $1 \rightarrow 0$, and the $1 \rightarrow 0$ spectrum is seen with its expected hyperfine structure, leaving no doubt as to the reality of the identification. The abundance ratio DCN/HCN deduced from comparison with $HC^{13}N$ and HCN^{15} is 1/170.

This D/H ratio is 40 times greater than the value in terrestrial water and 100 times greater than D/H observed in methane (CH_4) from Jupiter's atmosphere. It is also about 80 times greater than the limit Sander Weinreb obtained in 1962 for interstellar atomic deuterium in the direction of the radio source Cass A. This extremely large abundance of deuterium cannot be accounted for by any known process of element formation, including stellar nucleosynthesis or a big-bang model. The largest fraction of deuterium that can be produced in a big-bang model, constrained by the observed density of the universe and temperature of the background radiation, is approximately D/H equal to 10^{-5}. Deuterium is burned at a temperature of about 8×10^5 K, so that any cycling through stars can only reduce the D/H ratio.

The contradiction between the observed and expected values of D/H might be explained by one of two possibilities: Deuterium production may take place in Galactic objects under conditions never previously considered, or the observed ratio may be peculiar to hydrocyanic acid and not at all representative of the true D/H ratio. Although the first possibility would indeed be the more interesting, the latter may play a substantial role in accounting for the observations. In particular, the zero-point vibrational energy of DCN is much lower than that of HCN; the difference is 598 cm^{-1}, E/k = 861 K. Therefore in chemical reactions at low temperatures, the fraction of deuterium forming hydrocyanic acid may be greater than the fraction for hydrogen.[25]

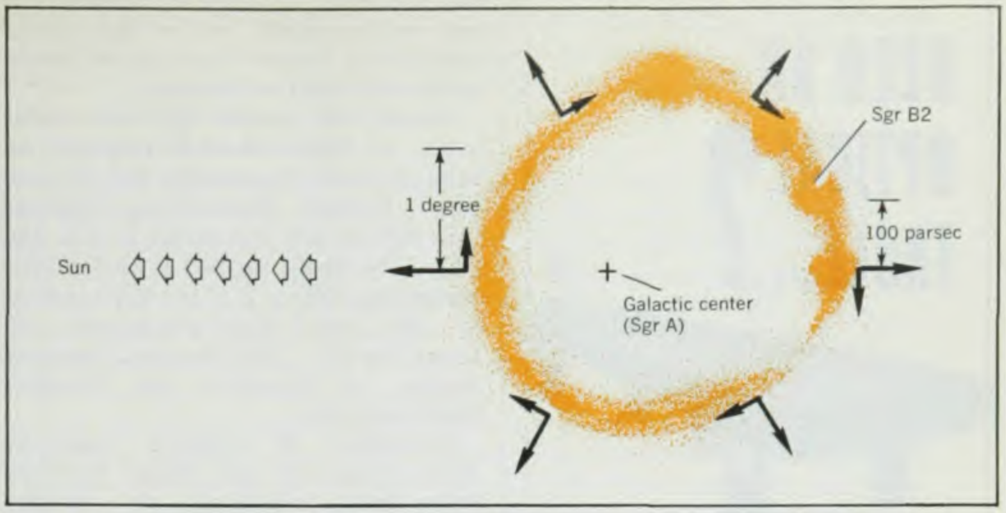
The most important reactions determining the degree of this chemical "fractionation" involve either H_2 and HD, or H and D. If most of the deuterium is in molecular hydrogen, as appears likely, then chemical exchange on the surface of interstellar dust (which is probably the site of formation of polyatomic molecules) through the reaction

$$HD + HCN \rightleftharpoons H_2 + DCN$$

will lead to an abundance ratio

$$\frac{DCN}{HCN} = \frac{HD}{H_2}\exp\left(\frac{456}{T}\right) = \frac{2D}{H}\exp\left(\frac{456}{T}\right) \quad (9)$$

where 456 K is the net excess binding energy of DCN + H_2 compared to HCN + HD. The temperature of the dust grains as determined from infrared observations is about 80 K, so



Motion of molecular clouds, observed to be expanding out from the Galactic center, is seen in this schematic drawing. CO emission from throughout this region is observed, showing a continuous structure that agrees with this interpretation (see reference 10, 1972). Expansion velocity is about 100 km per sec. From reference 20. Figure 5

that equation 9 yields a true deuterium abundance D/H of about 10^{-5}. Thus chemical fractionation of deuterium can be very substantial if reactions occur at low temperatures. Even greater fractionation will take place in exchange reactions between atomic deuterium and hydrocyanic acid. (Further evidence for the presence of deuterated molecules is the recent detection, from the Orbiting Astronomical Observatory, of ultraviolet absorption lines due to HD in several low-density clouds.[26])

A probable detection[27] of the 92-cm radio line from atomic deuterium in the interstellar medium, at a level $2 \times 10^{-5} < D/H < 5 \times 10^{-4}$, is consistent with the above observations. However, a deuterium fraction greater than 10^{-5} or so can be accounted for by synthesis in the big bang only for an "empty" universe ($q_0 = 0$, $\rho \sim 2 \times 10^{-31}$ gms/cm^3): A new type of astronomical object or event may be required to account for the observed deuterium abundance.

Interstellar chemistry

There are two classes of theory for the formation of interstellar molecules. In the first, the molecules are formed in and expelled from stellar or protostellar envelopes. In the second, local formation is constantly taking place in the clouds where molecules are found. The first mechanism has the advantage of formation in a medium with sufficiently high density (about 10^{14} cm^{-3} for hydrogen) for three-body gas-phase reactions to take place. These processes, which dominate "laboratory" chemistry, will lead to a rich chemical mixture with relative abundances governed by simple thermodynamic equilibrium. However, destruction of molecules by photodissociation due to starlight takes place on a time scale of 10^2 to 10^4 years. The presence of molecules such as CH, CH^+ and CN in regions transparent to starlight (and therefore subject to rapid photodissociation) means that at least these species are forming locally. In addition, the vast extent of clouds observed by microwave lines, containing at the very least CO, OH and H_2CO, suggests that molecules are very widely dispersed, and not likely to have survived a journey from a star, lasting 10^5 or 10^6 years, to reach their current location. Local formation is therefore required.

The physical conditions for interstellar formation of molecules are far removed from thermodynamic equilibrium. At the low density (less than 10^6 cm^{-3}) compared to terrestrial chemistry, present even in the regions of highest interstellar density, the time scale for three-body gas-phase reactions is greater than the age of the universe. Chemical reactions are therefore limited to either two-body gas-phase processes or reactions taking place on the surface of interstellar dust particles.

A complete theory must account for the rich variety of molecules that have been observed (see Table 1). In considering the chemistry it is also important to know what molecules are not present. However, observers are usually reluctant to report negative results, which are frequently difficult to interpret in terms of upper limits on abundance, particularly for complex molecules. For example, many observers have searched for and not found ring molecules such as ethylene oxide or pyridine, even though measured laboratory frequencies are available. Ring molecules are probably less abundant than other organic heavy molecules already detected, such as cyanoacetylene (HC_3N),[28] methyl alcohol (CH_3OH)[29] or methyl cyanide (CH_3CN),[16], all of which are well known to organic chemists. The question of how far chemical evolution in the interstellar medium has proceeded towards biochemistry is not yet answered, but it has clearly gone much further than anyone would have estimated five years ago.

Among the simple diatomic molecules, we have obtained negative results at radio frequencies for NO and SO. Optical observations indicate that NH is low compared to CH and CN. The result for NO is particularly interesting ($NO < 3 \times 10^{-3}CO$) in view of the very high abundance obtained for CO. The chemical processes leading to formation are therefore highly selective.

Formation of diatomic molecules from atoms by gas phase reactions have been considered by William Klemperer and me.[30] In interstellar clouds of low or moderate density, these gas-phase reactions produce a substantial abundance of several important species. The direct formation from atoms to molecules takes place by two-body radiative recombinations of C and H or C^+ and H to form CH and CH^+. Consideration of over 40 total processes including photodissociation, recombination, charge exchange and chemical exchange reactions leads to the additional production of CN, CO and C_2 but not NO, N_2 or O_2. The most abundant constituent predicted is CO, and reasonably good agreement is obtained with optical observational abundances of CN, CH and CH^+ for clouds at least partially transparent to radiation. Thus many simple molecules can be accounted for by specific gas-phase reactions.

At this time there is no quantitative theory for formation of polyatomic molecules. General considerations of reactions on grain surfaces[31] and physical absorption processes indicate that large numbers of polyatomic molecules *could* form on grain surfaces, but specific predictions cannot yet be made because reactions on grain surfaces and even the nature of the grain surface is only poorly understood. It is clear, however, from the observations that interstellar chemistry is a young and exciting field requiring new insights into the basic understanding of chemical reactions.

References

1. W. S. Adams, Astrophys. J. **109**, 354 (1948).
2. S. Weinreb, A. H. Barrett, M. L. Meeks, J. C. Henry, Nature **200**, 829 (1963).
3. C. H. Townes in *Proceedings* of the Fourth Symposium of the International Astronomical Union, (H. C. Van de Hulst, ed.) 1957, page 92.
4. A. C. Cheung, D. M. Rank, C. H. Townes, D. C. Thornton, W. J. Welch, Phys. Rev. Lett. **21**, 1701 (1968); Nature **221**, 626 (1969).
5. C. Heiles, Astrophys. J. **151**, 919 (1968).
6. P. M. Solomon, N. C. Wickramasinghe, Astrophys. J. **158**, 449 (1969); D. Hollenbach, M. W. Werner, E. E. Salpeter, Astrophys. J. **163**, 165 (1971).
7. L. E. Snyder, D. Buhl, B. Zuckerman, P. Palmer, Phys. Rev. Lett. **22**, 679 (1969); B. Zuckerman, D. Buhl, P. Palmer, L. E. Snyder, Astrophys. J. **160**, 485 (1970); P. Palmer, B. Zuckerman, D. Buhl, L. E. Snyder, Astrophys. J. **156**, L147 (1969).
8. A. A. Penzias, R. W. Wilson, Astrophys. J. **142**, 419 (1965).
9. R. W. Wilson, K. B. Jefferts, A. A. Penzias, Astrophys. J. **161**, L43 (1970); A. A. Penzias, K. B. Jefferts, R. W. Wilson, Astrophys. J. **165**, 229 (1971).
10. P. M. Solomon, N. Z. Scoville, A. A. Penzias, R. W. Wilson, K. B. Jefferts, Astrophys. J. **178**, 125 (1972); N. Z. Scoville, P. M. Solomon, Astrophys. J. **180**, 55 (1973).
11. P. M. Solomon in *Proceedings* of the 1971 National Radio Astronomy Observatory Symposium on Interstellar Molecules (M. A. Gordon, ed.) Wiley, New York (1973); A. A. Penzias, P. M. Solomon, R. W. Wilson, K. B. Jefferts, Astrophys. J. **174**, L43 (1972).
12. A. A. Penzias, P. M. Solomon, R. W. Wilson, K. B. Jefferts, Astrophys. J. **168**, L53 (1971).
13. P. Thaddeus, R. W. Wilson. M. Kutner, A. A. Penzias, K. B. Jefferts, Astrophys. J. **168**, L59 (1971).
14. L. E. Snyder, D. Buhl, Astrophys. J. **163**, L47 (1971).
15. A. H. Barrett, P. R. Schwarz, J. W. Waters, Astrophys. J. **168**, L101 (1971).
16. A. C. Cheung, D. M. Rauk, C. H. Townes, W. J. Welch, Nature **221**, 917 (1969).
17. P. M. Solomon, K. B. Jefferts, A. A. Penzias, R. W. Wilson, Astrophys. J. **168**, L107 (1971).
18. B. J. Robinson, R. X. McGee, Austr. J. Phys. **23**, 405 (1970).
19. N. Z. Scoville, P. M. Solomon, P. Thaddeus, Astrophys. J. **172**, 335 (1972).
20. N. Z. Scoville, Astrophys. J. **175**, L127 (1972).
21. A. A. Penzias, K. B. Jefferts, R. W. Wilson, H. S. Liszt, P. M. Solomon, Astrophys. J. **178**, L35 (1972).
22. R. W. Wilson, A. A. Penzias, K. B. Jefferts, P. Thaddeus, M. Kutner, Astrophys. J. **176**, L77 (1972).
23. V. J. Bortolot, P. Thaddeus, Astrophys. J. **175**, L17 (1972); P. A. Vanden Bout, Astrophys. J. **176**, L127 (1972).
24. K. B. Jefferts, A. A. Penzias, R. W. Wilson, Astrophys. J. **179**, L57 (1973); R. W. Wilson, A. A. Penzias, K. B. Jefferts, P. M. Solomon, Astrophys. J. **180**, 15 March (1973).
25. P. M. Solomon, N. J. Woolf, Astrophys. J. **180**, L89 (1973).
26. L. Spitzer, in *Proceedings* of the 1973 New Mexico Meeting of the AAS.
27. D. A. Cesarsky, A. T. Moffet, J. M. Pasachoff, Astrophys. J. **180**, L1 (1973).
28. B. Turner, Astrophys. J. **163**, L35 (1971).
29. J. A. Ball, C. Z. Gottlieb, A. E. Lilley, H. E. Radford, Astrophys. J. **162**, L203 (1970).
30. P. M. Solomon, W. Klemperer, Astrophys. J. **178**, 389 (1972).
31. W. D. Watson, E. E. Salpeter, Astrophys. J. **175**, 659 (1972). □