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Interstellar Molecules and Dense Clouds

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The large variety of molecules, including complex organic ones, recently discovered in interstellar space shows such regions to be much richer in composition than had generally been expected from earlier observations. The diatomic species CN, CH, and CH^+ were discovered in the ultraviolet just before 1940, and OH was found at 18 centimeters in the radio spectrum in 1963. Since the discovery of radio emission from the polyatomic molecule NH_3 in late 1968, radio observatories have devoted considerable time to searches for additional molecules, and the list of molecules now detected has grown to almost 20, including altogether: CN, CH, CH^+, H_2, OH, NH_3, H_2O, H_2CO, CO, CS, SiO, OCS, HCN, CH_3CN, HNCO, HC_3N, HCOOH, CH_3OH, NH_2HCO, and at least one unidentified species. Hydrogen molecules were detected in the far ultraviolet by rocket, the other new molecules by radio telescope.

These discoveries bear directly on a number of interesting questions and raise still others. They provide, of course, new knowledge about the composition of the universe. Further, although the molecules are trace constituents, typically less than one part per million of neutral hydrogen, the study of their excitations and abundances gives important measures of the present physical conditions and of the history of gas and dust clouds between the stars. Some molecules may also play an important role in the radiative cooling of these clouds. One wonders further how the molecules are formed and what their lifetimes are. Are they blown out from the atmospheres of stars, formed by successive binary collisions, or by chemical processes on the dust grains? If the latter, how do they then get away from the grains? The state of excitation of these molecules provides information on radiation intensities in their vicinities. Finally, these observations have an interesting connection with biology. Mixtures of such molecules as H_2O, HCN, NH_3, and H_2CO are common starting points for primitive earth synthesis experiments to examine possible processes that can initiate life. In such experiments, HC_3N and HNCO are typical important products, which can play a role in further synthesis. Even though the interstellar molecules may not survive the violence of the birth of a solar system and hence may not occur initially in primitive planetary atmospheres, the fact that such molecules can form in the apparently hostile interstellar environment supports the view that they (and more complicated ones) can readily be formed in planetary atmospheres.

Before these recent findings are reviewed in any detail, it will be useful to recall some of the general properties of the interstellar medium. Apart from the stars, the major constituent of the galaxy is neutral hydrogen, which has an average density over the whole galaxy of about one atom per cubic centimeter. On a large scale, the gas and stars appear to be organized into a spiral structure similar to that of the great galaxy in Andromeda. The entire structure rotates, though not like a rigid body, about its center, with the rotational velocity about 250 kilometers per second at the distance of our sun from the galactic center.

On a smaller scale, the distribution of matter is irregular, with gas and dust grains concentrated into relatively cool, dense regions or clouds surrounded by less dense, hotter gases. The clouds occupy 5 to 10 percent of the volume of our galaxy. Differences among the clouds are considerable; sizes vary from perhaps 0.1 to 50 light years and gas densities from about 10 to greater than 10^5 cm^{-3}. Kinetic temperatures range from 20° to 200°K within most of the clouds, and turbulent velocities vary from a few tenths to about 20 km/sec. The dust grains are small, of the order of a few tenths of a micron, and of uncertain composition. Typically about 1 percent of the cloud mass is in the grains, so that there is one dust grain for about every 10^{12} hydrogen molecules. The gas density between the clouds is of the order of 0.1 cm^{-3}, with temperatures in the range of 100° to 1000°K or more. The electron density averaged over the entire galaxy is about 0.05 cm^{-3}, but it may be largely concentrated in the less dense regions. The average density of heavier atoms is 10^{-3} cm^{-3} or less.

No single temperature can describe the galactic radiation field. The average field consists of two principal components: dilute starlight and the isotropic microwave background. The former radiation has a color temperature of about 10,000°K, but corresponds to blackbody radiation at this temperature reduced in intensity by a factor of 10^{14}. The latter radiation, usually interpreted as a residue from the primeval fireball, lies mostly in the microwave range and corresponds approximately to that of a blackbody at 2.7°K. Both components have about the same energy density.

The galaxy is also pervaded by high energy particles or cosmic rays. These are largely protons and heavy nuclei with energies up to 10^{20} electron volts per nucleon and an energy spectrum

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that follows approximately a power law down to a few million electron volts. The energy density of all such particles is about 10^{-12} erg cm^{-3}, comparable to the energy density of the electromagnetic radiation; the majority of the energy is due to the particles in the lower energy range of the spectrum. The more energetic cosmic-ray electrons, gyrating in magnetic fields of a few microgauss average intensity, produce the synchrotron radiation that illuminates the galaxy in the radio range at wavelengths longer than about 30 cm.

The brightest stars, with surface temperatures greater than 10,000°K, emit sufficient ultraviolet light to completely ionize the hydrogen in their neighborhoods. These ionized regions, called H II regions, frequently are the large diffuse nebulae that can be seen in photographs of the Milky Way. One of the brightest of these is the great nebula in the sword of Orion; it stands out against a dark dust cloud that obscures the light from the stars beyond. Many of the recently discovered molecules can be found in the direction of this nebula.

Various selection effects, both natural and human, influence the study of interstellar molecules. The observer must contend with a number of natural circumstances. To begin with, the earth's atmosphere is transparent for only part of the electromagnetic spectrum. Atmospheric gases cut off transmission at wavelengths short of the 3,000- to 10,000-Å visible "window"; infrared transmission is fairly good in a number of bands between 1 and 14 microns, but the atmosphere is rather opaque from 14 microns to 1 millimeter. Except for a few specific regions shorter than 1 cm where H_2O or O_2 absorb, the transmission is good from 1 mm out to a few meters, where the ionosphere becomes opaque. The majority of observations are still made from the ground and must employ these "windows." The recent development of rocket, balloon, and satellite techniques has begun to make the rest of the spectrum available.

The various molecular transitions occur in characteristic regions of the spectrum: electronic transitions in the visible and ultraviolet, pure vibrational transitions in the infrared, and pure rotational transitions generally in the far infrared and short microwave. At longer radio wavelengths the fine structure, hyperfine, and lambda and *K* doubled transitions are most important. Because collisions with particles and photons occur infrequently, the molecules or atoms are usually in a low state of excitation, except in the H II regions. Thus, an electronic transition can be seen only as an absorption feature produced by a foreground cloud in the spectrum of a background star. On the other hand, a hyperfine transition arising between levels near the ground state may produce measurable microwave emission from the whole of the molecular cloud. One other difficulty in the study of molecules in the visible part of the spectrum is the general extinction of starlight by the dust, particularly in the near ultraviolet. Because of this, it is difficult to observe material that is more distant than 3000 light years. Infrared and radio waves are not so affected by the dust, and at any wavelength longer than the near infrared one can study clouds in more distant regions of the galaxy. On the other hand, the longer wavelengths usually provide poorer angular resolution, and the typical radio telescope provides very fuzzy pictures of spatial distributions.

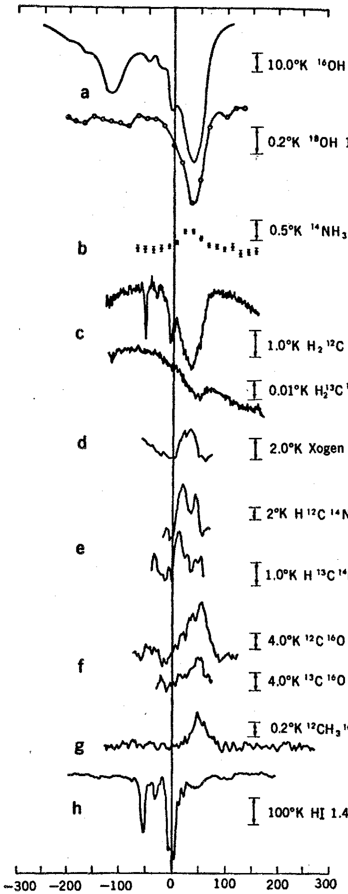

Fig. 1. Microwave spectra taken in the direction of the center of our galaxy. The frequency scale has been converted to a scale of radial velocity, V_R, with respect to the rest frame of stars near the sun, in accordance with the Doppler formula. Spectra come from the following sources: a (*54*), b (*21*), c (*90*), d (*22*), e (*93*), f (*38*), g (*95*), h (*107*).

In the radio region normal stars emit too little radiation to be detected by the average radio telescope, and the background sources that are used for observation of absorption in foreground molecular clouds are the extended supernova remnants and H II regions, or the general background of synchrotron radiation. These sources have brightness temperatures that decrease with decreasing wavelength, and at wavelengths shorter than about 1 cm there are few sources with enough intensity to be used as background sources for absorption observations. Hence, in the region between 1 cm and 1 mm where many of the interesting rotational transitions lie, one can study only those molecular transitions that are sufficiently excited to emit significantly.

Not surprisingly, many of the line discoveries have been made possible by the improvement in radio telescopes in recent years, particularly at the shorter wavelengths. Both the improvement in basic receiver sensitivity and the development of spectroscopic equipment for short wavelengths have played an important role.

Frequently, only one or a few spectral lines are observed in the radio region for a given molecule. The total number of molecular lines of appropriate intensity and the high precision with which their frequencies can be measured, however, usually leave little doubt about positive identification of the molecular species responsible, as long as the line signal is sufficiently strong that it is clearly detected above noise. As the result of extensive laboratory measurements during the last 25 years, the microwave spectra of most of the relatively simple molecules with appreciable vapor pressures have been identified and cataloged (*1*), with the result that about 10,000 lines per frequency octave are known in the more intensively explored parts of the microwave region. Interstellar lines are usually measured to a precision of about one part in 20,000 and sometimes much more precisely. This implies that not more than one or two known frequencies are likely to agree randomly with the measured frequency in such a way as to confuse the identity of the line source. In addition, the vast majority of molecular lines known from laboratory studies are due to molecules that would be very rare in interstellar space, or almost anywhere else. Identification is aided further by the fact that many of the lines occur in closely spaced or related groups associated with hyperfine structure (see Fig. 2d), rotation-vibration interactions, or rare isotopes. Thus, the presence of one such line with or without other related lines gives further easy criteria for identification. In general, detection of a single line that is well above noise and agrees with a known molecular resonance has allowed an identification that can hardly be questioned. Frequently more than one line associated with a given molecule is found, in which case the identification, even on the basis of frequency criteria alone, is usually incontrovertible. In cases so far reported, there has been no uncertainty due to the near coincidence of molecular lines, with the exception of NH_2HCO, whose lines are more or less coincident with H recombination lines, and HCOOH, whose resonance is near resonances of ^{18}OH. Since the latter transitions are also observed, the HCOOH line is apparently distinguishable.

Optical Identification of Interstellar Molecules

In the late 1930's, Dunham and Adams (*2*) at Mount Wilson observed a number of bright blue stars in the ultraviolet with high resolution and discovered several sharp interstellar absorption lines that were subsequently identified with the diatomic species CH^+, CH, and CN (*3–5*). This was the first evidence of molecules in the interstellar medium. Although the lines were faint, Adams was able to detect them in about 25 percent of some 300 bright stars that he observed in various directions. This showed that the distribution of such molecules is widespread.

The early identifications were based on at least two lines for each diatomic molecule, and other predicted lines have been found subsequently. The line-of-sight Doppler velocities of the molecular components correspond closely to those of interstellar atomic Na and Ca in front of each star—an indication that the atoms and molecules coexist in the same regions. The atomic lines are stronger, and when they are observed with very high resolution (*6*) they separate into several components at different wavelengths. These components are generally interpreted as representing the different Doppler velocities of discrete clouds along the line of sight.

Many more of the stars show absorption by CH and CH^+ than by CN. This might be expected because H is cosmically about 10^4 times more abundant than N. However, in those stars that do show CN the CN absorption is comparable with that of the CH, and, because the oscillator strengths of the transitions are similar, the abundances are comparable (*7*). In these cases, the chemistry within the cloud must play a dominant role in determining the molecular abundances. The column densities are typically 10^{12} cm^{-2} for both CH and CN. The mean molecular densities between the sun and the star are then typically 10^{-9} cm^{-3}, and, if one takes into account the fact that the gas is mostly in clouds, the densities are about 10^{-8} cm^{-3} in the clouds.

The presence of dust in the interstellar medium is shown directly by the reddening of starlight due to scattering by the dust particles. On the whole, the strengths of the molecular lines correlate with the amount of reddening for most of the stars. This indicates that the amounts of dust and of molecules are correlated and that the dust probably occurs in the clouds containing molecules. However, there are some stars closer to the sun that show little reddening but do show traces of interstellar CH^+ and CH. For these stars, the relative velocities between the stars and the molecular clouds suggest that the clouds are close to the stars and may even surround them.

With one exception, the molecular absorptions are due to electronic transitions from the ground state to various excited vibrational states. This is evidence of the general low level of excitation of the interstellar material. The exceptional case is CN, which shows transitions from the first excited rotational state lying 3.78 cm^{-1} above the ground rotational state. From the ratio of the excited to the ground state line intensities that Adams observed in the star Zeta Ophiuchi, McKellar (*5*) derived a rotational temperature of 2.3°K for the interstellar medium (*4*). The significance of this temperature was not fully appreciated until after the discovery of the universal microwave 2.7°K background radiation by Penzias and Wilson in 1965 (*8*). Field and Hitchcock (*9*) and Clauser and Thaddeus (*10*) have reexamined the excitation in Zeta Ophiuchi and a number of other stars and found general agreement between the rotational temperatures and the direct microwave measurements (*11*). The CN rotational temperatures are a measure of the background radiation field at a wavelength of 2.6 mm.

Further searches in the optical spectrum of stars have produced no additional sharp lines that could be identified with spectral lines of simple molecules such as OH or NH (*12*). The one exception appears to be Bortolot and Thaddeus' (*13*) recent discovery in the spectrum of Zeta Ophiuchi of a faint line slightly displaced from a line of $^{12}CH^+$. They attribute the feature to the corresponding line of $^{13}CH^+$ and derive a value of about 82 for the isotopic ratio $^{12}C:^{13}C$. This ratio is close to the terrestrial value.

In 1936, Merrill (*14*) reported the detection of a broad, diffuse interstellar line or band at 4427-Å wavelength (*15*). Subsequently, more such features have been discovered at a number of wavelengths. Although a number of suggestions have been advanced, no fully satisfactory identification has yet been made for any of these features. Herzberg (*16*) has proposed that these may be due to some molecular species with resonances broadened by predissociation. Johnson (*17*) found that some of these resonances correspond to frequencies of a magnesium porphyrin, though whether this molecule can be responsible for the observed spectra is not yet clear.

Rocket techniques, which permit observations in the extreme ultraviolet part of the spectrum from above the atmosphere, have recently made possible the detection of ultraviolet absorption by both H_2 and CO. Carruthers (*18*) observed the stars Epsilon and Xi Persei and detected strong absorption by the Lyman resonance bands of H_2 in the latter star; he derived a column density of 4×10^{19} cm^{-2} for H_2 molecules. No H_2 absorption appeared in the spectrum of the former star. The extinction of starlight, presumably by dust, is about 75 percent toward the star that shows H_2 as compared to about 25 percent toward the other—indicating the expected correlation between the presence of H_2 and the amount of dust.

Smith and Stecher (*19*) have reported ultraviolet absorption by interstellar CO in the direction of one star, Zeta

Ophiuchi. They estimated a column density of about 7×10^{15} molecules cm^{-2}, much greater than the density of CN or CH but several orders of magnitude less than the amount that has been observed in the radio spectrum in the direction of, for example, the Orion nebula. They also detected $^{13}C^{16}O$ and obtained for the isotopic ratio ^{12}C:^{13}C about 105, close to the terrestrial value.

Radio Molecular Lines

It was not until 25 years after the detection of molecular lines in the optical region and 12 years after the discovery of the 21-cm atomic hydrogen line that the first molecule, OH, was detected in the interstellar medium by radio telescope. Lines at 18 cm corresponding to absorption between Λ doublets of the ground state of the OH molecule were detected against a number of galactic continuum radio sources by Weinreb *et al.* (*20*) in 1963. Five years later, NH_3 molecules were detected by Cheung *et al.* (*21*) with the observation of emission lines at a wavelength of 1.25 cm. Since then, the list of molecules that have been observed by radio telescope has been expanding at an ever increasing rate. Table 1 is a list of the molecular resonance lines in the radio frequency region that have been observed in our galaxy up to mid-1971. About 50 lines from at least 19 molecular species have been detected. Two lines for which no definite identification is yet possible have been detected at wavelengths near 3 mm (*22, 23*). One of these (*22*) has been dubbed xogen until a suitable identification is found. Presumably it is a molecule or radical that is short-lived and rare under laboratory conditions, so that its spectrum is not yet known. The second unidentified line seems uncorrelated in intensity distribution with the first and presumably is due to a distinct molecular species. The frequencies of these molecular resonances span nearly the whole radio frequency region of the electromagnetic spectrum from 36-cm to 2-mm wavelength. While Table 1 contains many simple molecules such as OH, CO, and CN, it also contains rather complex ones such as HC_3N and CH_3OH in substantial abundance.

The frequency of an interstellar line can be measured extremely accurately, which allows small shifts in frequency due to the Doppler effect to be detected easily. Most normal interstellar radio lines have widths about 10^{-4} to 10^{-5} of their frequencies. Hence, Doppler shifts as small as 10^{-5} of the velocity of light, or 1 km/sec, are detected easily. This allows precise determinations of radial velocity for molecular gas clouds in the galaxy. Velocities for such clouds with respect to the sun range up to a few hundred kilometers per second. In general, the spiral arms of the galaxy tend to rotate approximately uniformly, and models of uniform rotation for the galaxy can hence associate distances with radial velocities measured in certain directions. In addition to this general motion, individual clouds have their own specific velocities with respect to the rotating galaxy. Thus, the Doppler shift, or the frequency shift of a resonance line from its laboratory value, can be associated with particular clouds of gas and specific locations in our galaxy. This Doppler shift can in principle give some uncertainty to the molecular frequency and hence to its identification. However, the shifts are not very large and are usually reasonably well known from other lines found in the same region of space.

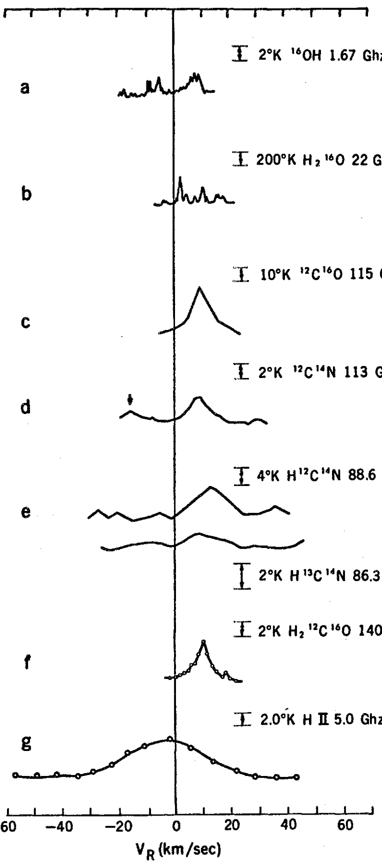

Fig. 2. Microwave spectra taken in the direction of the Orion nebula. As in Fig. 1, the horizontal scale represents radial velocity V_R. Spectra come from the following sources: a (*104*), b (*108*), c (*89*), d (*92*), e (*93*), f (*89*), g (*109*). The symbol *H II* indicates a line resulting from recombination of an electron with ionized hydrogen.

Figure 1 shows the spectra of a number of molecules that are detected in the direction of the center of our galaxy. Figure 1h is the spectrum of neutral hydrogen 21-cm absorption against the strong radio source Sagittarius A, which is located at the center of our galaxy. The central region or core of the galaxy may be responsible for absorptions at 0 km/sec (no radial velocity), or they may be due simply to very local gas. The stronger absorptions with little Doppler shift probably represent the latter case. The feature at −55 km/sec and possibly also that at −30 km/sec are produced by the intersection of two spiral arms with our line of sight to the galactic center. It is immediately apparent from Fig. 1 that the strongest features in the molecular spectra of Sagittarius A do not correspond with the three strongest ones in the spectrum of atomic hydrogen. While OH and H_2CO show definite velocity features that correspond to the 21-cm hydrogen spectrum, the strongest concentration of molecules is in the range of velocities 25 to 75 km/sec, where there is a rather weak atomic hydrogen absorption feature. This suggests two quite different types of gas clouds. One is represented by the sharp features, which follow the atomic hydrogen closely, while the other shows a marked diminution of the atomic hydrogen intensity relative to the intensity of molecular lines typified by the broad features at 50 km/sec in Fig. 1. Presumably the ratio of total hydrogen abundance to the abundance of the other elements such as C, N, and O is the same for both. Hence, molecular formation is much more favored in the latter, where most of the atomic hydrogen has been replaced by molecular hydrogen. The density in such clouds is generally much greater than in clouds where the hydrogen is largely atomic; this is consistent with greater molecular formation and excitation. It is interesting to note that the maxima of the different molecular lines in Fig. 1, a–h, do not coincide exactly in velocity. This effect probably reflects the tendency of differences in the formation and excitation conditions to favor emission or absorption from different molecules in slightly different positions within the cloud.

Spectra of the Orion nebula (Fig. 2) show again that many of the molecules such as CO, CN, and HCN, are displaced slightly in velocity from the peak of 109 α hydrogen recombination radiation (Fig. 2g); this indicates that the molecules and the ionized hydrogen probably do not exist in the same regions of this gas cloud.

Soon after the detection of 18-cm (1665-megahertz) OH absorption, Weaver *et al.* (*24*) observed strong OH emission lines associated with H II regions in the galaxy. Spectral features from the Orion nebula (Fig. 2) illustrate this type of OH emission. The OH spectral lines are substantially narrower than the usual line widths resulting from turbulent velocities associated with galactic gas clouds. In addition, most features exhibit strong polarization, high

Table 1. Observed microwave resonances from interstellar molecules. Transition types are indicated by Λ for Λ doublet, ID for inversion doublet, and R for rotational. A plus sign indicates that the hyperfine structure (Hfs) has been detected. Emission and absorption are denoted by E and A, respectively.

Discovery	Molecule	Rotational quantum numbers	Transition type	ν (Ghz)	Hfs	Spectrum	Reference
1963	$^{16}OH(^2\pi_{3/2})$	$J=3/2$	Λ	1.665	+	E, A	(*20, 24, 78*)
1969		$=5/2$	Λ	6.035	+	E	(*79*)
1970		$=7/2$	Λ	13.441		E	(*80*)
1968	$^{16}OH(^2\pi_{1/2})$	$J=1/2$	Λ	4.766		E	(*81*)
1969		$=5/2$	Λ	8.136		E	(*82*)
1966	$^{18}OH(^2\pi_{3/2})$	$J=3/2$	Λ	1.637	+	A	(*52*)
1968	$^{14}NH_3$(para)	$(JK)=1,1$	ID	23.694		E	(*21, 83*)
	(para)	$=2,2$	ID	23.723		E	(*83*)
	(ortho)	$=3,3$	ID	23.870		E	(*83*)
	(para)	$=4,4$	ID	24.139		E	(*83*)
	(ortho)	$=6,6$	ID	25.056		E	(*83*)
1969	$H_2{}^{16}O$ (ortho)	$J_{K_{-1}K_1}=5_{23}-6_{16}$	R	22.235		E	(*84*)
1969	$H_2{}^{12}C^{16}O$(ortho)	$J_{K_{-1}K_1}=1_{11}-1_{10}$	R	4.830	+	A, E	(*85, 86*)
		$=2_{12}-2_{11}$	R	14.488		A	(*87*)
		$=3_{13}-3_{12}$	R	28.974		A	(*88*)
1971	$H_2{}^{12}C^{16}O$(ortho)	$=1_{11}-2_{12}$	R	140.839		E	(*89*)
	$H_2{}^{12}C^{16}O$(para)	$=1_{01}-2_{02}$	R	145.603		E	(*32*)
	$H_2{}^{12}C^{16}O$(ortho)	$=1_{10}-2_{11}$	R	150.498		E	(*32*)
1969	$H_2{}^{13}C^{16}O$(ortho)	$=1_{11}-1_{10}$	R	4.593		A	(*90*)
1970	$^{12}C^{16}O$	$J=0-1$	R	115.271	None	E	(*91*)
1971	$^{13}C^{16}O$	$J=0-1$	R	110.201		E	(*38*)
1971	$^{12}C^{18}O$	$J=0-1$	R	109.782	None	E	(*38*)
1970	$^{12}C^{14}N$	$J=0-1$	R	113.492	+	E	(*92*)
1970	$H^{12}C^{14}N$	$J=0-1$	R	88.632	+	E	(*93*)
1970	$H^{13}C^{14}N$	$J=0-1$	R	86.339	+	E	(*93*)
1970	Xogen (unknown, possibly HCO^+)			89.190		E	(*22*)
1970	$H^{12}C_3{}^{14}N$	$J=0-1$	R	9.098	+	E	(*94*)
1970	$^{12}CH_3{}^{16}OH$	$J_{K_{-1}K_1}=1_{11}-1_{10}$	R	0.834		E	(*95*)
1971	$^{12}CH_3{}^{16}OH$	$(JK)=4,1-4,2$	R	24.933		E	(*96*)
		$=5,1-5,2$	R	24.959		E	(*96*)
		$=6,1-6,2$	R	25.018		E	(*96*)
		$=7,1-7,2$	R	25.125		E	(*96*)
		$=8,1-8,2$	R	25.294		E	(*96*)
1970	$H^{12}C^{16}O^{16}OH$	$J_{K_{-1}K_1}=1_{11}-1_{10}$	R	1.639		E	(*97*)
1971	$^{12}C^{32}S$	$J=2-3$	R	146.969	None	E	(*98*)
1971	$^{28}Si^{16}O$	$J=2-3$	R	130.268	None	E	(*99*)
1971	$^{12}CH_3{}^{12}C_2H$(ortho)	$(JK)=4,0-5,0$	R	85.457		E	(*23*)
1971	$H^{14}N^{12}C^{16}O$	$J_{K_{-1}K_1}=3_{03}-4_{04}$	R	87.925		E	(*23*)
		$=0_{00}-1_{01}$	R	21.982		E	(*23*)
1971	$^{16}O^{12}C^{32}S$	$J=8\text{-}9$	R	109.463	None	E	(*100*)
1971	$^{12}CH_3{}^{12}C^{14}N$(ortho)	$(JK)=5,0-6,0$	R	110.384		E	(*101*)
	(para)	$=5,1-6,1$	R	110.381		E	(*101*)
	(para)	$=5,2-6,2$	R	110.375		E	(*101*)
	(ortho)	$=5,3-6,3$	R	110.364		E	(*101*)
	(para)	$=5,4-6,4$	R	110.349		E	(*101*)
	(para)	$=5,5-6,5$	R	110.330		E	(*101*)
1971	X_2(unknown, possibly HNC)			90.665		E	(*23*)
1971	$^{14}NH_2H^{12}C^{16}O$	$J_{K_{-1}K_1}=2_{12}-2_{11}$	R	4.619	+	E	(*102*)
1971	CH_3HCO	$J_{K_{-1}K_1}=1_{10}-1_{11}$	R	1.065		E	(*103*)

brightness temperatures ($\gtrsim 10^9$ °K), and rapid intensity fluctuations. These characteristics are evidence for a nonthermal population distribution of the molecular states, corresponding to a population inversion and hence maser action, which will be discussed in more detail below. In addition to the ground state of OH, H_2O and some excited rotational states of OH show maser action in astronomical sources. The H_2O maser action so far detected always occurs in sources that show OH maser emission as well. However, many OH masers show no detectable H_2O emission. The H_2O emission from such clouds is less polarized than that of OH and frequently more intense, with brightness temperatures up to 6×10^{13} °K.

A number of observational patterns characteristic of the masers have emerged. In most cases, maser action is associated with three general classes of astronomical objects: (i) H II regions, (ii) supernova remnants, and (iii) certain infrared stars. The OH maser action tends to be most intense for the 1665- or 1667-Mhz hyperfine line near H II regions and for the 1612-Mhz hyperfine line in infrared stars (*25*). More rarely the 1720-Mhz component can be the most intense. The Doppler shift, polarization, and intensity fluctuations of excited state OH masers often correlate with those of the ground state radiation from the same region. Intensity fluctuations of H_2O radiation can occur in periods of weeks, while OH radiation fluctuates more slowly.

Although the OH also appears in emission and absorption in extended regions, the H_2O only appears in emission from very small, bright regions. This is not unexpected, since the H_2O transitions are between rather highly excited states that decay too rapidly to be abundant in the rarefied environment of extended clouds. Efforts to determine the sizes of the small radiating regions of OH and H_2O have led, finally, to Very Long Baseline Interferometry (VLBI) involving both continental and intercontinental baselines (*26*). This technique employs independent, precision, reference oscillators and high-speed tape recorders at two widely separated observing stations; signals received from a given radio source are independently recorded at the two stations and combined later in a digital computer to form a long baseline Michelson interferometer. The longest baseline used for these studies extended from Hat Creek, California, to Onsala, Sweden (*27*). Because the radio frequency signals are recorded on high-speed magnetic tape, the effective observing time is very limited, and only the few strongest sources have so far been studied in any detail by this technique.

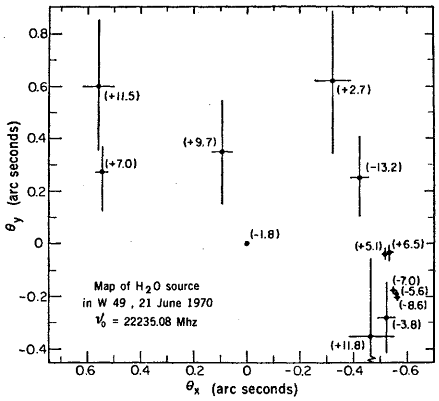

Fig. 3. Map of H_2O maser sources in W49. Positions relative to the −1.8 km/sec feature and upper limits to the uncertainty in the relative position of each source are shown [from Johnston *et al.* (*26*)]. The velocity of each feature in kilometers per second is given in parentheses. The symbols θ_x and θ_y represent angular displacements in the directions of increasing right ascension and declination respectively.

Observations of the small OH emission regions show the following general picture. In each region there are one or more clusters of small sources; the clusters are separated by a few tens of arc seconds, and the individual cluster size is typically 1 arc second. Each cluster contains several very small sources with each corresponding to a different Doppler feature in the overall emission spectrum of the source. The features are often completely circularly or linearly polarized. There is no obvious correlation between position and line-of-sight velocity of the sources within the cluster. At present, the absolute positions of the clusters are known only within a few arc seconds, so that they cannot be accurately located with respect to optical objects or other radio objects as yet. The sizes of the individual sources are in the range 0.005 to 0.05 arc second, with those in the most distant regions having the largest angular sizes. The true source sizes may be much smaller, as the apparent sizes may be due to scattering of the 18-cm radiation by irregularities in the free electron density in the interstellar medium.

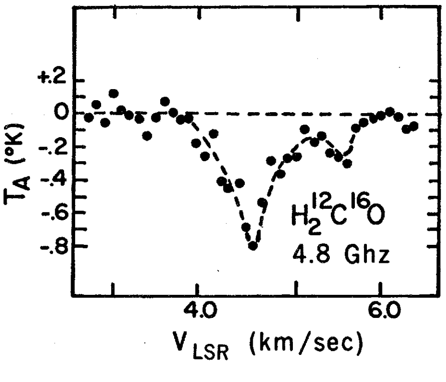

Fig. 4. H_2CO absorption spectrum in the direction of a dark cloud in the galaxy, from Palmer *et al.* (*29*). The cloud itself produces no detectable continuum radiation; hence, the spectrum represents absorption of the 2.7°K isotropic radiation. The symbol T_A represents the antenna temperature, and V_{LSR} is the velocity along the line of sight referred to the local standard of rest.

The H_2O sources in the same regions as the OH sources generally have many similar properties and a few important differences. In the most distant region, W49 for example, about a dozen features with line-of-sight velocities in the range − 15 to + 15 km/sec lie within a circle of angular diameter about 1.0 arc second, as shown in Fig. 3. The velocities are referred to the local standard of rest (LSR), which is stationary with respect to the center of mass of stars near the sun. In this complex, the individual features are as yet unresolved, as their angular diameters are less than 0.0005 arc second, which corresponds to a linear dimension of 8 astronomical units at the large distance of this region. Within observational error, about 10 arc seconds at the present writing, the H_2O sources lie in the same direction as one group of OH sources in W49. The brightness temperature of the brightest of these features is greater than 5×10^{13} °K. Only one H_2O source has been resolved so far, a feature in the direction of the Orion nebula. This source has an angular size corresponding, at the distance of the Orion nebula, to a linear dimension of about 0.4 astronomical unit, a dimension approaching the size of a large star.

The increase produced in apparent source size by electron scattering is proportional to λ^2, where λ is the wavelength. This effect would therefore be less by a factor of 200 for the H_2O emission than for OH. The smaller H_2O source sizes are indeed consistent with this interpretation.

Many of these observational results for OH can be explained by theoretical models that involve infrared, ultraviolet, or collisional excitation, and subsequent radiation. The probable nature of such masers will be discussed below.

Several other molecules exhibit nonthermal population distributions that are not accompanied by maser action. There is a substantial difference between the rotational temperatures of the ortho and para species of NH_3 (*28*), orthoammonia being approximately 50°K hotter than paraammonia in one case. This nonequilibrium is very likely due to the very long time constant associated with ortho to para conversion. The excitation of H_2CO is rather remarkable in certain very dense clouds. The molecule appears not to be in equilibrium with the isotropic 2.7°K radiation but is cooler (*29*). Figure 4 is a spectrum of the H_2CO ground state absorption from one such cloud. The cloud in this case produces no continuum radiation at 4000 Mhz. Hence, the molecule must be absorbing radiation from the isotropic blackbody continuum, and the effective temperature of the two states is lower than 2.7°K. This observation demonstrates the universality of the blackbody radiation, at least on a galactic scale, and H_2CO should be a very useful tool for its study. The spectrum of CH_3OH, which is shown in Fig. 1g, has not been detected in absorption even against very strong continuum sources, where the background temperature is about 300°K. It may also be exhibiting some stimulated emission, though the evidence for this is inconclusive.

The distribution of molecules in interstellar space is clearly not random. All molecules detected to date are within our galaxy, except for the recently reported detection of OH in M82 and NGC253 (*30*). The distribution within our galaxy is strongly concentrated toward the galactic plane. Figure 5, a map of the celestial sphere, shows the positions of all known concentrations of interstellar molecules; the U-shaped curve represents the intersection between the celestial sphere and the galactic plane. The high density of molecules in the galactic plane is very evident, especially toward the galactic center, where the bulk of the total mass of the galaxy is concentrated. If the molecules were a local phenomenon concentrated in the region of our galaxy near the sun, their distribution on the celestial sphere would be essentially uniform and would present a very different picture in Fig. 5. Since the sun lies very close to the galactic plane, Fig. 5 gives a measure of the distance from the sun to the molecular clouds. The greater the distance from the sun to a cloud, the higher the probability is that the cloud lies near the intersection of the galactic plane and the celestial sphere. It is therefore possible to obtain a rough estimate of the distance of some clouds from the sun simply by knowing their positions in the sky. A more detailed measure of distance can be obtained by comparing the Doppler shift of a molecular spectral line with the shifts of known hydrogen lines in the same direction.

Molecules as Probes of Interstellar Clouds

The detection of molecules and the measurement of their spectral parameters yield, as has been seen above, direct information on the constitution, location, and velocities of molecular clouds. Interpretation of the measured parameters in the light of other knowledge can provide a wealth of information about the origin, conditions, and dynamics of the gaseous concentrations in interstellar space. The latter is indirect information and hence less certain than the first three properties mentioned above. However, a few aspects of interpretation can be made with reasonable surety now. Other parts will be clarified by more extensive and careful astronomical measurements or by laboratory investigations, while still other aspects must remain uncertain until there are further discoveries, perhaps by quite different techniques. In any case, observations of molecules in space will probably make their greatest contribution to astronomy in this indirect way, through the use of the very specific information the resonances provide about conditions where the molecules are found. Molecular resonances can be considered as probes of the interstellar medium in much the same sense that nuclear resonances, after their first discovery, became used primarily as probes of the materials in which the nuclei are imbedded. Possible interpretations of molecular resonance observations are explored below; it will be clear that many questions are still unsettled.

Because molecular excitation in interstellar space does not usually correspond to thermal equilibrium, the intensities of molecular emission or absorption lines are frequently not simple to interpret; yet, also because of this, each intensity measurement can yield independent and useful information. The state of molecular excitation is determined by a combination, and frequently a competition, of interactions with particles and with radiation. The particles include neutral molecules, whose kinetic energy is usually in the range of a few tens of degrees, and electrons, which may be at a somewhat higher temperature. The radiation in-

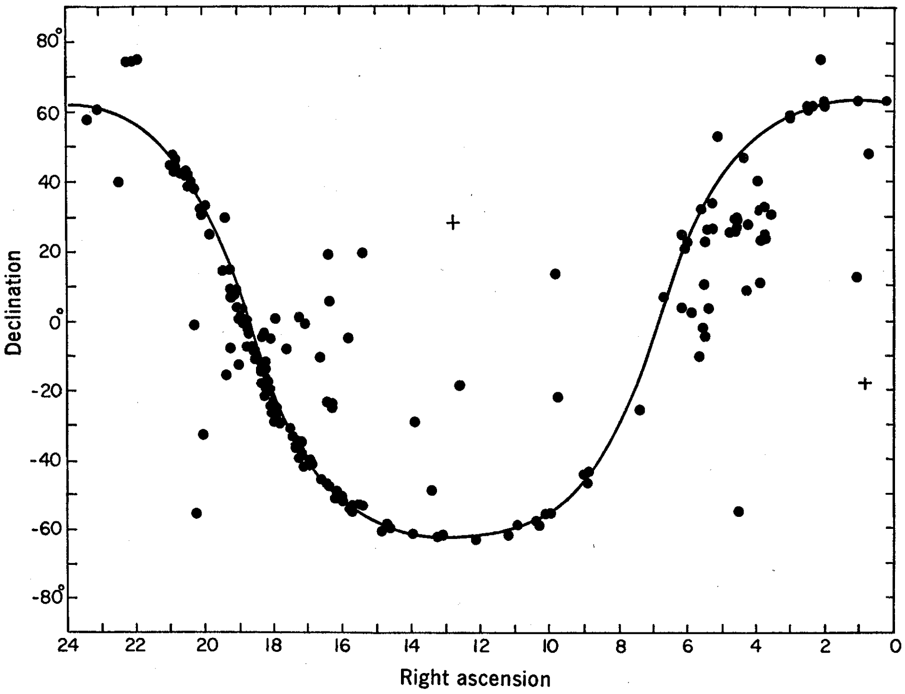

Fig. 5. Map of the celestial sphere with the distribution of galactic sources that show molecular lines. The map is a rectangular projection of right ascension and declination coordinates; the galactic plane is represented by the solid line. [Courtesy of M. F. Chui]

cludes the isotropic background radiation, approximately blackbody radiation at 2.7°K, and more local resonant or continuum radiation, which may represent a much higher temperature. In cool dust clouds, interactions with the isotropic radiation and collisions with neutral molecules are most certainly present, and frequently they are in close enough competition that it is uncertain whether a given molecular resonance should be in equilibrium with the radiation and hence at a temperature of 2.7°K, or with the molecular kinetic energy and hence at some tens of degrees. As a result of both influences, a given pair of energy states may have an inverted population and give maser action, or it may be cooled even below 2.7°K.

The most directly determinable rate of relaxation between two molecular states is that due to the isotropic radiation, which, combined with spontaneous emission, tends to bring the molecular population into equilibrium with the radiation temperature; the time constant for relaxation, $\tau_r/2$, corresponds to an effective transition rate

$$\frac{1}{\tau_r} = \frac{64\pi^4\nu^3|\mu|^2}{3hc^3\,(1 - e^{-h\nu/kT})} = \frac{8}{3h}\left(\frac{2\pi}{\lambda}\right)^3 \frac{|\mu|^2}{(1 - e^{-h\nu/kT})} \qquad (1)$$

where h is Planck's constant, c is the speed of light, and k is the Boltzmann constant; $|\mu|$ is the molecular dipole matrix element for the transition, λ is its wavelength, and ν its frequency; T is the temperature of the isotropic radiation, approximately 2.7°K. The transition time τ_r is found to be in the range 10^5 to 10^{10} seconds, or of the order of years, for most microwave transitions.

The rate of transition due to collisions may be written

$$\frac{1}{\tau_c} = \sum_m (n\sigma v)_m \qquad (2)$$

where the subscript m indicates a given species of colliding particle, n is its density, σ is the effective cross section for producing a transition, and v is the average relative velocity of the two colliding particles. The cross section σ applies to a particular transition.

For neutral molecules, σ can be estimated simply from molecular dimensions to be of the order of 10^{-15} cm^2; in certain cases this cross section has been measured in the laboratory, and a reasonably precise value is available (*31*). Since the cosmic abundance of hydrogen is about six times that of helium and more than 10^3 times that of any other element, we may assume that the majority of collisions made with neutrals is with hydrogen atoms or molecules; thus, only one or two terms of Eq. 2 are of importance, and it can often be approximated simply as $1/\tau_c = n\sigma v$, where n is the total particle density. The cross sections for various neutrals do not differ greatly; a rather extreme variation is, for example, the difference between NH_3-NH_3 collisions, where $\sigma = 2 \times 10^{-14}$ cm^2 for the 3,3 inversion line, and NH_3-He collisions, where $\sigma = 5 \times 10^{-16}$ cm^2. For electrons or positive ions, the cross section depends strongly on the electrical properties of the molecule. If it has a dipole moment μ, a rough value is $\sigma \approx \mu e/\hbar v$, where e is the electric charge and $\hbar = h/2\pi$. For normal dipole moments and a frequency ν in the microwave range, $\sigma \approx 10^{-11}$ cm^2, which is very much larger than the cross section for neutral molecules.

Table 2. Densities of H_2 molecules that give equal collisional and radiational transition rates for various spectral lines (see Eq. 4). The observation of these lines in emission, or in absorption against the isotropic microwave radiation, implies either minimum densities comparable with these values or the presence of electrons in abundance greater than 10^{-5} of the same values.

Molecule	Resonant frequency (Mhz)	H_2 density (cm^{-3})
H_2CO	4,829.73	10^2
H_2CO	140,839	3×10^5
NH_3	23,694.48	10^3
CO	115,271.2	2×10^3
HCN	88,631.87	10^6

If transitions between an upper and a lower molecular level are produced only by collisions with particles at temperature T_m and radiation at temperature T_r, then the effective temperature of the two levels is

$$T_{eff} = \frac{\tau_r T_m + \tau_c T_r}{\tau_r + \tau_c} \qquad (3)$$

Here it is assumed that $h\nu \ll kT$, where ν is the transition frequency and T any of the above temperatures; this assumption is usually good but needs modification in a few cases of interest. The fractional difference in population of the two levels is $h\nu/kT_{eff}$, which is a definition of T_{eff}. From Eq. 3, if the radiation temperature produced by molecules is to be substantially different from the temperature T_r of the isotropic radiation, which it must be for the resonances to be seen against this background alone, τ_c must not be very much larger than τ_r. Thus, any observation of molecular emission implies that the states are not in equilibrium with the isotropic radiation and that collisions or some other radiative excitations are frequent enough to be important.

The density of particles that would make τ_c just equal to τ_r is given, from Eqs. 1 and 2, by

$$n = \frac{64\pi^4|\mu|^2}{3h\lambda^3\sigma v(1 - e^{-h\nu/kT})} \qquad (4)$$

Assuming a typical dipole matrix element $\mu \approx 10^{-18}$ electrostatic units and neutral molecules of normal cross section $\sigma = 10^{-15}$ cm^2 and velocity $v = 10^5$ cm/sec, this gives

$$n = \frac{3 \times 10^3}{\lambda^3(1 - e^{-h\nu/kT})} \qquad (5)$$

For very short microwaves, where $h\nu \gg kT$, the factor in parentheses is near unity. For longer waves, it is approximately $h\nu/kT$, which is not usually less than about 1/10. Equation 5 implies that a rather high density of molecules, which must be primarily H_2, exists in dust clouds (*21, 32*). Furthermore, the density required to produce emission lines increases rapidly with decreasing wavelength. For a few specific molecules, Table 2 shows the implications of Eq. 5.

Whether electron collisions play an important role in exciting many of the observed molecular microwave transitions is not entirely clear, although they are probably much less important than neutral collisions in the dense dust clouds. When little dust is present, short ultraviolet and other ionizing radiation can produce electrons in some abundance, and they would contribute importantly to collisions. However, in these regions such radiation also dissociates molecules very rapidly. One can expect that molecules are typically seen only where the ultraviolet is substantially screened out by dust. Inside the dust clouds, the electron abundance depends crucially on the poorly known cosmic ray spectrum, particularly that in the energy range 1 to 20 Mev, and on the density of molecules, which produce recombination of the electrons and ions.

The relative abundance of electrons to molecular and atomic hydrogen can be judged from Fig. 6, where population ratios, given by Solomon and

Werner (*33*), are plotted as a function of the ratio of ionization rate to the total particle abundance, ζ/n. In free space, this ionization rate ζ is approximately 10^{-15} cm^{-3} sec^{-1} (*34*). Whether it is due to soft x-rays or cosmic rays with energy a few million electron volts or lower is not known. Soft x-rays would not penetrate dust clouds appreciably. Low energy cosmic rays would be more penetrating but would not traverse dense dust clouds. The maximum and minimum electron densities given in Fig. 6 are based, respectively, on the assumptions that all the carbon is atomic and ionized or that it is completely un-ionized. Since hydrogen atoms are relatively nonabundant and combined into molecules, it is reasonable to assume that ionized carbon atoms are rare. On this basis, the curve for the ratio of electron density to hydrogen atom density, n_e/n_H, is drawn. Even if relatively high ionization rates occur within a dust cloud, Fig. 6 shows that the low atomic hydrogen ($\lesssim$ 1 cm^{-3}) observed in many clouds is not consistent with electron densities sufficiently high ($\gtrsim$ 10^{-2} cm^{-3}) for the latter to be a dominant factor in collisional excitation of molecules. Rather, the dominant species in dense dust clouds is expected to be molecular hydrogen. This conclusion is especially clear when the observed microwave spectra of molecules require very rapid collisional excitations, which imply densities of 10^5 neutral molecules per cubic centimeter or more.

The densities of molecular hydrogen given in Table 2 would give, following Eq. 3, molecular excitation temperatures just halfway between the kinetic temperature and the 2.7°K of isotropic radiation, if only two molecular levels are involved importantly in establishing their relative populations. While the densities of molecular hydrogen need not have these precise values, they cannot be very much less because this would imply temperatures too close to 2.7°K to allow observation of resonant emission above the isotropic background. Observations of molecular resonance lines, other than as absorption by gas in front of an intense continuous source, thus show that the molecules detected occur in regions of high molecular density. The HCN lines and the 2-mm wavelength (~140,000-Mhz) transitions of H_2CO require surprisingly high densities, near 10^6 cm^{-3}.

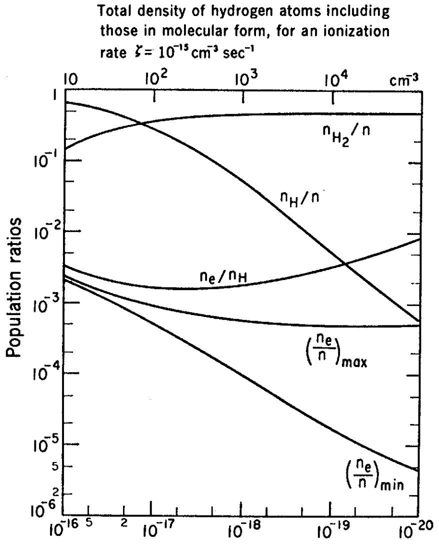

Fig. 6. Relative abundance of hydrogen molecules, hydrogen atoms, and electrons in the presence of ionization [after Solomon and Werner (*33*)].

While the densities given in Table 2 are approximate lower limits only, upper limits are probably not very much higher because of the very large masses and gravitational instabilities this would imply. For example, if the Sagittarius B2 cloud is a few light years in diameter as expected and of density 10^6 cm^{-3}, it should contain about 10^5 solar masses. The time for collapse of a cloud of density ρ by free fall is approximately $t \approx 1/(\rho G)^{\frac{1}{2}}$, where G is the gravitational constant. For a density of 10^6 hydrogen molecules per cubic centimeter, this time is only 30,000 years. Molecular velocities found in clouds do often indicate adequate turbulence or rotational motion to prevent such rapid collapse, but probably many local instabilities occur within the cloud. There is, indeed, considerable evidence that densities in dust clouds are quite nonuniform. This comes, for example, from observations that amounts of absorption, or opacity, due to various microwave molecular resonances in a given cloud are much more nearly equal than can be expected simply from the relative abundances of the various molecular states. Such results are easily explainable by the presence of patches in the cloud that are optically very dense and others that are much less dense. A region checkered with very dense small clouds unresolved by the antenna beam, for example, could give much the same apparent optical density for both strong and weak resonant transitions. Inhomogeneities on a larger scale are easily seen by examination of molecular velocities and column densities as a function of angle with a narrow antenna beam (*35, 36*).

The number of molecules that produce a given resonant line can usually be calculated with reasonable accuracy from the total absorption coefficient through a gas cloud, $\int\int \gamma ds d\nu$, where γ is the fractional absorption per unit distance at a given frequency ν, and ds an element of distance along the line of sight. From well-known expressions for the absorption coefficient,

$$\int\int \gamma d\nu ds = \frac{8\pi^3}{3hc} |\mu|^2 \nu \int (n_L - n_U) ds \quad (6)$$

where n_L and n_U are the densities of molecules in the lower and upper states respectively, and $|\mu|$ the dipole matrix element for the transition. If the molecular distribution is represented by a uniform temperature T and if $h\nu \ll kT$, as is typical for microwave frequencies, then $n_L - n_U = Nh\nu/kT$, where N is the density of molecules in both states, and Eq. 6 becomes

$$\int\int \gamma d\nu ds = \frac{8\pi^3 |\mu|^2 \nu^2}{3ckT} \int N ds \quad (7)$$

For most normal line shapes, $\int \gamma d\nu \approx \gamma_{max}\Delta\nu$, where λ_{max} is the peak absorption and $\Delta\nu$ is the total width at half maximum, so that this integral is easy to estimate.

The total column density of the molecules in these two states is given by the integral $\int N ds$ and can often be evaluated from Eq. 7. For absorption of an intense continuum after it has traversed a cloud, the integrated absorption coefficient can be evaluated, but the temperature T is not usually well known and must be estimated. For direct emission from a cloud, the apparent temperature of the radiation is $T_a = T(1 - e^{-\int \gamma ds})$, which for $\int \gamma ds \ll 1$, gives the result

$$T_{a,max}\Delta\nu \approx \int T_a d\nu = \frac{8\pi^3 |\mu|^2 \nu^2}{3ck} \int N ds \quad (8)$$

where $T_{a,max}$ is the peak temperature of the line. Thus, in this case the excitation temperature of the molecules need not be known in order to evaluate the column density $\int N ds$ directly from the measured quantity $\int T_a d\nu$.

Observed column densities of molecules in Sagittarius B2 (*37*), a dense cloud toward the center of the galaxy, and in the direction of the Orion nebula are listed in Table 3. Molecular densities may be obtained from these column densities by estimation of the size of the clouds. Thus, if the clouds are 10 light years in extent, the density of a particular molecular species is the column density divided by 10^{19}. For reasons indicated above, values of column densities are generally rather accurately known if the molecule is seen in emission, and less accurately known if it is seen in absorption, since in the latter case intensity is critically dependent on an assumed temperature (usually 10° to 100°K). If the molecule is seen through maser action alone, as is H_2O, no real measurement of column density is obtainable.

From Table 3 and other evidence, one concludes that most of the gaseous material in dense clouds is in the form of relatively simple molecules. A comparison of the numbers of these molecules with the amount of hydrogen thought to be present in such clouds indicates that at least a substantial fraction, of the C, O, and N that the clouds contain must be accounted for by the observed species (*21*). In some cases, the amount of CO observed contains even more C and O than has been thought available (*38*). The small abundance of atomic hydrogen compared with molecular hydrogen has been discussed above. The simple free radicals OH and CN coexist with less reactive molecules, but Table 3 shows them to be relatively rare compared with the more stable diatomic molecule CO and not substantially more abundant than the more complex species HCN, HN_3, or H_2CO. Molecular abundance tends to decrease with increasing number of atoms in the molecule. However, many molecules are detected near the limit of present sensitivity. This tends to set lower limits on column densities so far discovered and to leave little doubt that many additional and more complex species remain to be found by sensitive methods.

If the molecular gas were in thermodynamic equilibrium, the intensity of microwave radiation would set a lower limit to its temperature. In many cases this intensity corresponds to a temperature of only about 1 degree above the temperature of the isotropic radiation, because the cloud of gas is not optically thick. Furthermore, thermodynamic equilibrium is not assured. One case where it is tempting, and might be correct, to associate the molecular radiation temperature with the kinetic temperature of the molecules is the 2.6-mm radiation from CO ($J = 1 \rightarrow 0$ rotational transition). In the direction of the Orion nebula, this radiation from $^{12}C^{16}O$ has a peak intensity corresponding to 40°K (*34*), and the cloud is almost certainly optically thick. In other directions corresponding to very dark, probably cool, clouds, this peak is as low as 2 degrees (*39*) above the isotropic radiation. The normally much less abundant $^{13}C^{16}O$ has an intensity in both cases about one-third that of $^{12}C^{16}O$, which gives some indication that the cloud is optically thick (*38*, *39*). If the collisions were very rapid compared to radiative transitions, this measurement would then indicate the very low kinetic temperature of about 8°K. However, it is not certain that

Table 3. Present estimates of column density (number of molecules per square centimeter) along the line of sight, for molecules found in the directions of Sagittarius B2 and the Orion nebula. The density of H_2 is inferred from excitation processes (see Eq. 4 and Table 2). Other column densities come primarily from integrated line intensities (see Eq. 8).

Molecule	Column density in Sgr B2 (cm^{-2})	Column density in Orion (cm^{-2})	Comment	Reference
H_2	$\geq 10^{22}$	$\sim 2 \times 10^{23}$	Indirect determination	(*83, 32*)
OH	$> 5 \times 10^{16}$	?	*T* assumed 29°K for Sgr B2; primarily maser radiation from Orion	(*54, 104*)
CO	$\sim 10^{19}$	$\sim 10^{18}$	Optically dense clouds, hence column density uncertain	(*38, 91*)
CN	Not detected	$\sim 10^{15}$	*T* assumed 50°K	(*92*)
CS	$\sim 10^{14}$	2×10^{13}—5×10^{14}		(*98*)
SiO	$\sim 4 \times 10^{13}$	Not detected	*T* assumed 30°K	(*99*)
H_2O	?	?	Maser radiation	(*84*)
HCN (hydrogen cyanide)	Not determined	$\sim 10^{15}$	*T* assumed 20°K for Orion	(*93*)
OCS (carboxyl sulfide)	$\geq 3 \times 10^{15}$	Not detected		(*100*)
NH_3 (ammonia)	$\geq 10^{17}$	Not detected	*T* assumed 35°K	(*83*)
H_2CO (formaldehyde)	$\sim 2 \times 10^{15}$	$\sim 3 \times 10^{14}$	*T* assumed 3°K	(*32, 105*)
HNCO (isocyanic acid)	Not determined	Not detected		(*23*)
HC_3N (cyanoacetylene)	$\sim 2 \times 10^{16}$	Not detected	*T* assumed 50°K	(*94*)
HCOOH (formic acid)	10^{13}—3×10^{15}	Not detected	Line interfered with by ^{18}OH transitions	(*97*)
CH_3OH (methyl alcohol)	?	$\sim 5 \times 10^{16}$	Cloud sizes unknown; possibly maser radiation from Sgr B2; very small cloud in Orion	(*95, 96*)
CH_3CN (methyl cyanide)	$\sim 2 \times 10^{14}$	Not detected		(*101*)
CH_3C_2H (methyl acetylene)	Not determined	Not detected		(*23*)
Xogen (unknown)	Not detected	$\sim 10^{15}$	Frequency 89, 190 Mhz; rough estimate of abundance	(*22*)
X_2 (unknown)	Not detected	Not detected	Frequency 90, 665 Mhz; found in sources W51 and DR21	(*23*)
NH_2HCO (formamide)	Not determined	Not detected		(*102*)

collisions are overwhelmingly frequent and that the cloud is uniformly optically thick, so that these temperatures must be subject to further examination.

There are at least four temperatures in an interstellar cloud that are important in discussing molecular resonances. These are the kinetic temperatures of the gas, the excitation temperature for the relative populations of two energy levels of interest, the temperature of the dust grains, and the radiation temperature. Because thermodynamic equilibrium is unlikely, usually no two of these temperatures are the same. However, if collisions were much less frequent than transitions induced by the 2.7°K isotropic radiation, then the excitation temperature would be that of the isotropic radiation, and, as noted above, no radiation from the molecular resonance could be detected. If collisions are much more frequent, then the excitation temperature approaches that of the kinetic motion.

The NH_3 inversion emission at about 1.25 cm richly illustrates temperature and excitation considerations and perhaps provides our best indicator of kinetic temperature. Rotation and inversion levels for NH_3 are shown in Fig. 7. The inversion transitions, corresponding to the molecule turning inside out like an umbrella, are between the closely spaced doublets in Fig. 7 and occur at slightly different frequencies for each rotational level because of centrifugal effects. The levels with no angular momentum about the symmetry axis ($K = 0$) show no inversion. Almost all close collisions can produce transitions between the two inversion levels. Somewhat less commonly they change the total angular momentum J by one unit, and still less commonly they change K by three units or J by an amount larger than unity. The transition probabilities for inversion levels, a unit change in J, or a change in K are roughly in the ratio 1:(1/10):(1/100) for collisions between He or H_2 and NH_3 (*40*). The distributions of mass and charge for the two inversion levels are so nearly identical that the relative excitation of any pair as a result of a collision probably depends only on their small difference in energy, so that they come to equilibrium with the kinetic energy on each collision. Furthermore, the cross section for H_2-NH_3 collisions for producing such transitions has the relatively large value 3×10^{-15} cm^2 (*31*).

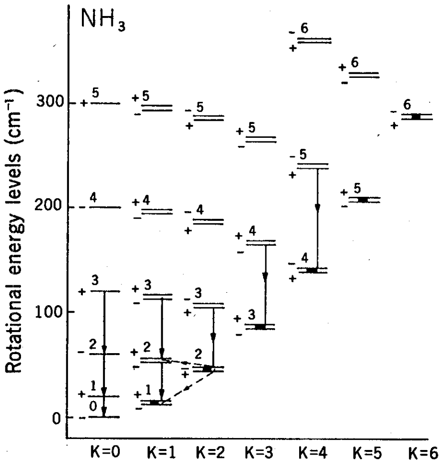

Fig. 7. Energy level diagram for NH_3. Rotational and inversion levels are shown with allowed transitions. The angular momentum around the symmetry axis, *K*, is indicated along the horizontal axis. The total angular momentum, *J*, is given next to each level. Positive and negative signs indicate parity of the states.

By contrast with the above case, neither collisions nor radiation can produce appreciable transitions between rotational states with $K = 3n$ and those with $K = 3m + 1$, where n and m are integers, including zero. These two groups of states involve a total spin for the three protons in NH_3 of 3/2 and 1/2, respectively, and their relation is much like that of ortho- and parahydrogen. They can come to equilibrium most easily through an exchange collision with a hydrogen atom, or through adsorption on the surface of a dust grain and reevaporation. Under conditions typical of dense interstellar clouds, either process would require times as long as about 10^6 years to equilibrate the two species (*35*).

All states with $J = K$ are metastable with respect to radiative transitions. Collisions are the primary source of transitions between these states; they produce fairly frequent transitions between states with $K = 3n + 1$ and $K = 3n - 1$ or between those with $K = 3n$, but essentially none between these two species, paraammonia and orthoammonia. Okla *et al.* (*41*) have shown that radiative transitions due to vibration-rotation perturbations do occur slowly between states of NH_3 with different K values. Such transitions are allowed only between states of the same species, that is paraammonia or orthoammonia. These authors estimate that the 3,3 level decays to the 2,0 level, for example, in 10^9 seconds—a time that is usually, but not necessarily always, sufficiently longer than the time between collisions that this process can be neglected. The fact that the 3,3 inversion radiation is observed shows that collisions must be more rapid than this rate, or hence that molecular densities are greater than about 100. This is consistent with the densities suggested in Table 2 but does not give substantial new information.

The relative populations of various rotational states of NH_3 seem to provide one of the best measures of kinetic temperature for the clouds in which NH_3 is found. It has been noted above that the relative populations of the two inversion states in each rotational level are very likely determined by the kinetic temperature; this ensures that the ratio of populations in the upper and lower inversion states is essentially the same in all rotational states, so that the relative intensities of inversion radiation for these states must accurately reflect the relative populations of rotational states. The population ratio between states 1,1 and 2,2, determined by collisions rather than any radiative processes, as a first approximation would be presumed to be given by

$$n_{11} = \frac{3}{5} e^{-\Delta w/kT} n_{22} \qquad (9)$$

where n_{11} and n_{22} are the densities in the two states, 3/5 is the ratio of statistical weights $(2J' + 1)/(2J + 1)$, and Δw is the energy difference of 30 cm^{-1}. This expression is probably not grossly in error. However, collisions can produce transitions from the 2,2 state to the 2,1 state as well as to the 1,1 state, and any molecule in the 2,1 state radiates quickly (~100 seconds) to the 1,1 state. Still other rotational states with $K = 1$ and with $K = 2$ may be involved in collisions and affect, by rapid radiative decay, the relative populations of the two metastable states 1,1 and 2,2. The expectation that for a given value of K higher rotational states have largely decayed to the lowest one has been checked by a search for inversion radiation of the 2,1 and 4,3 states; this was not found. Thus, the more precise steady state condition is

$$n_{11} \sum_J p_{11 \rightarrow J,2} = n_{22} \sum_J p_{22 \rightarrow J,1} \qquad (10)$$

where $p_{11 \rightarrow J,2}$ represents the probability of collisional excitation from the 1,1 state to the J,2 state. There is reason to believe (*41*) that $p_{11 \rightarrow 22}$ and $p_{22 \rightarrow 11}$

are rather larger than other terms in this expression, in which case it reduces to Eq. 9. However, the relative values of the various terms are not really known, and Eq. 10 strongly implies that any temperature deduced from Eq. 9 is somewhat lower than the actual kinetic temperature. Measurements in various directions toward the Sagittarius B2 cloud give values of kinetic temperature between 20° and 80°K (*35*).

Population of the 3,3 level of NH_3 allows determination of the temperature equilibrium between ortho- and paraammonia. The collisions that bring molecular populations in the 1,1 and 2,2 states to a steady state in about 10^7 seconds or one-third year (the time between collisions) are quite ineffective in making transitions between these states and the 3,3 state. Since the 3,3 state is orthoammonia and the other two are paraammonia, transitions must be produced between them by quite different mechanisms, requiring 10^6 years or perhaps longer to produce a steady state. Thus, the ratio of the population in the 3,3 state to that in the 1,1 or 2,2 states probably represents some temperature occurring in the cloud 10^6 years or more in the past, rather than present temperatures as given by the 1,1 to 2,2 population ratio. It may reflect simply an effective temperature when the NH_3 was created. Comparison of the 3,3 inversion intensity with that of the 1,1 state, in fact, shows different and characteristically higher temperatures than those indicated by the 1,1 and 2,2 intensities (*35*).

More precise and extensive interpretation of excitation of NH_3 and kinetic temperatures must wait for additional laboratory measurements of collisional cross sections, or for more extensive and precise measures of intensities in interstellar space for a variety of rotational states. The latter should not be very difficult, since inversion radiation has already been seen in the 4,4 and 6,6 states as well as the three states mentioned above. A preliminary map of molecular densities and temperatures in the prominent Sagittarius B2 cloud is shown in Fig. 8.

The care and detail with which excitation and relaxation mechanisms must be understood to be interpreted soundly in terms of conditions within a cloud are illustrated by several instances of molecules that are clearly far from thermal equilibrium for any temperature within the cloud. Radiations from OH and H_2O, for example, are very intense and emanate from very small sources (*26, 27*), which indicates radiation temperatures at least as high as 10^{13} °K. Formaldehyde in dark clouds produces a decrease in radiation intensity below that due to the 2.7°K isotropic radiation (*29*), which shows that the excitation temperature for its transition near the 6-cm wavelength must be lower than 2.7°K, the best estimate being about 0.8°K. This is lower than any other known temperature of the cloud and must, as are the masers, be due to some nonequilibrium pumping process—a heat machine that removes energy and refrigerates the H_2CO levels, in contrast to those that continuously provide energy for the OH and H_2O masers.

Several processes have been proposed that may cool the H_2CO levels to such low temperatures. One involves collision and then reradiation (*42*). The two levels involved in the transition are designated by the quantum numbers 1_{11} and 1_{10} and shown in the energy level diagram, Fig. 9. Levels on the left-hand side of this diagram correspond to paraformaldehyde and those on the right to orthoformaldehyde. Ordinarily, there are no transitions between these two groups. At least for fairly energetic collisions, excitations are favored between either member of the doublet 1_{11} and 1_{10} and the lower members of the higher pairs. For example, the collision more readily makes the excitation $1_{10} \rightarrow 3_{13}$ than $1_{10} \rightarrow 3_{12}$ for reasons connected simply with momentum and energy conservation. Radiative transitions allow the molecule to decay fairly rapidly, but from the lower level of one doublet it can decay only to the lower member of a lower doublet, so that after decay the lowest state 1_{11} must have a substantially larger population than the upper state of the same doublet. This corresponds to a low excitation temperature for the pair and illustrates a refrigeration engine operated by a heat source, which is the kinetic energy, and a heat sink, which is the radiation field. Another proposal is that the 2.7°K isotropic radiation does not correspond exactly to blackbody radiation (*43*) but is somewhat augmented at a frequency corresponding to the $1_{10} \rightarrow 2_{11}$ transition. The resulting increase in the induced transition rate between the 1_{10} and 2_{11} levels, further induced transitions between the levels 2_{11} and 2_{12}, and then

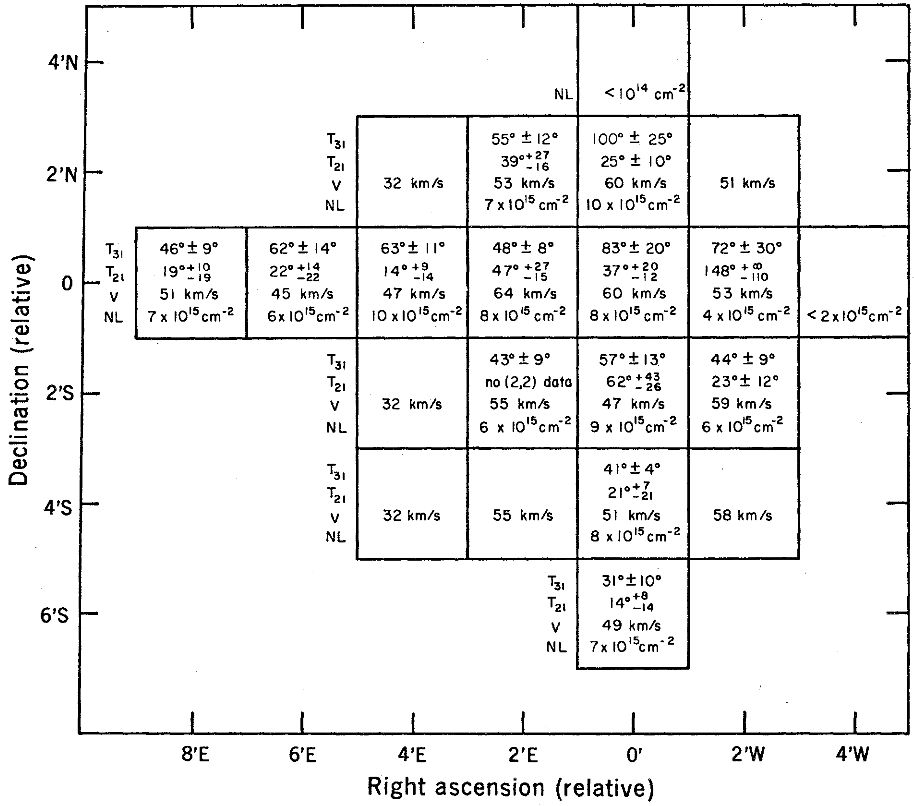

Fig. 8. Map of the densities, velocities, and temperatures of NH_3 in the direction of Sagittarius B2 [from Cheung *et al.* (*35*)]. The center of the coordinate system shown is $\alpha(1950) = 17^h44^m01^s$, $\delta(1950) = -28°21.6'$. The letters *NL* stand for the column density $\int N ds$ given in Eq. 7.

subsequent decay to the lowest doublet can also increase the population in the lowest state and hence cool the excitation temperature. Still another proposal involves radiative pumping by vibrational excitation of the H_2CO molecule (*44*). Which of these mechanisms actually applies is a subject of present investigations, and its resolution should provide further insight into conditions in these dark dust clouds.

As in the case of H_2CO refrigeration, a number of mechanisms have been proposed to pump molecules into the upper states of the H_2O and OH resonances—collisional pumping (*45*), radiation pumping (*46*), and various combinations. Considerations of these mechanisms are too detailed to discuss here. However, general properties of the H_2O and OH masers and of sources that produce them will be summarized.

The most striking aspect of radiation from H_2O at 1.35-cm wavelength and from OH at 18 cm is intensity, particularly the intensity per solid angle. Some OH sources show normal absorption and radiation, such as occur in a number of molecules. However, radiating OH sources are frequently intense enough to produce antenna temperatures close to 100°K for an 85-foot antenna, and H_2O sources give antenna temperatures as high as 6000°K. Furthermore, long baseline interferometry, the relatively new technique of examining the coherence of radiation received in two widely separated antennas, shows that the angular sizes of these OH and H_2O sources are exceptionally small—frequently at least as small as 10^{-8} radians, or still smaller and beyond the resolution of the best techniques available (*26, 27*). This implies radiation temperatures at the source that are greater than the antenna temperatures by the ratio of the antenna solid angle to the sources' solid angle, $<10^{-16}$ steradians, which for both OH and H_2O gives source temperatures as high as 10^{13} °K. Such temperatures clearly cannot be associated with kinetic energy of the molecules, nor with any radiation temperatures unless the radiation has been amplified. The latter implies maser action, with the necessary nonthermal distribution, a greater population being in the upper of the two states involved in the transitions.

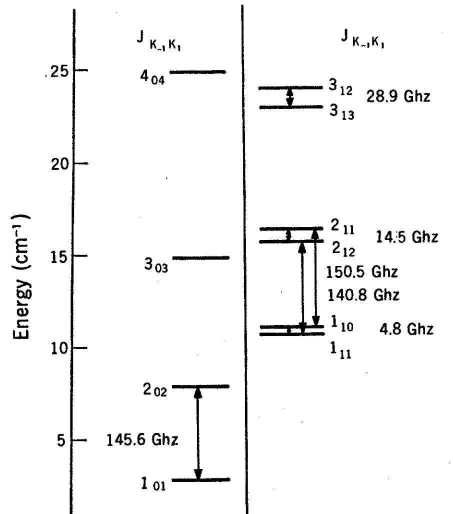

Fig. 9. Energy level diagram for the lower rotational levels of H_2CO. Levels are designated with the notation $J_{K_{-1}K_1}$ where J is the total angular momentum. K_{-1} and K_1 are angular momenta about the symmetry axes for the corresponding levels of a prolate and oblate symmetric top, respectively. The right-hand series of levels are those of orthoformaldehyde, and the left-hand series those of paraformaldehyde. Arrows show the transitions that have so far been observed from interstellar clouds.

The OH or H_2O maser radiation from a given source usually displays peaks at a number of different Doppler velocities, as illustrated by the H_2O spectrum of Orion shown in Fig. 2. Long baseline interferometry shows that in most cases each different Doppler velocity corresponds to a distinct small source, as indicated in Fig. 3 by the large group of closely spaced radiating sources in W49.

The actual frequency width of many of these peaks is as much as an order of magnitude less than the expected Doppler width, presumably because of narrowing due to gain. If the gain is large and there is no feedback or saturation of the molecular resonances, the line width should be reduced by the factor $[\ln (g/\sqrt{2})]^{-1/2}$ where g is the total gain. Saturation makes this factor nearer unity.

Other interesting features of OH and H_2O maser sources are their variability and polarization. Figure 10 shows the marked variations in the spectrum of H_2O in W49 from month to month; detectable variations occur at times in a few days (*47, 48*). Particular Doppler peaks in OH sources are frequently almost completely circular in polarization; others are partially linearly polarized. The H_2O masers are not known to show circular polarization, but there is linear polarization of about 10 percent in a few H_2O sources (*47*).

Stimulated emission can in principle have very different characteristics from thermal radiation; some of them are evident from the above discussion, and it is appropriate to examine what other peculiar characteristics may exist. The more intense sources, if they are more or less isotropic as seems likely, must be radiating a total power within the restricted frequency range of the microwave resonance as large as 10^{30} to 10^{33} ergs per second, which is comparable with the entire radiant energy of the sun. It has been suggested that galactic maser sources are highly directional, so that their apparent high intensities do not imply as much total power as would be expected from an isotropically radiating body. Such directionality cannot be completely ruled out. However, since a number of separate masers usually occur in a given small region, and since a very large fraction of the known H_2O masers also occur with OH masers, an assumption of high directivity requires that in most maser sources there are such large numbers of separate masers that the average radiated energy in any one direction is not much different from that in any other direction. The total radiation from the entire group of presumedly highly di-

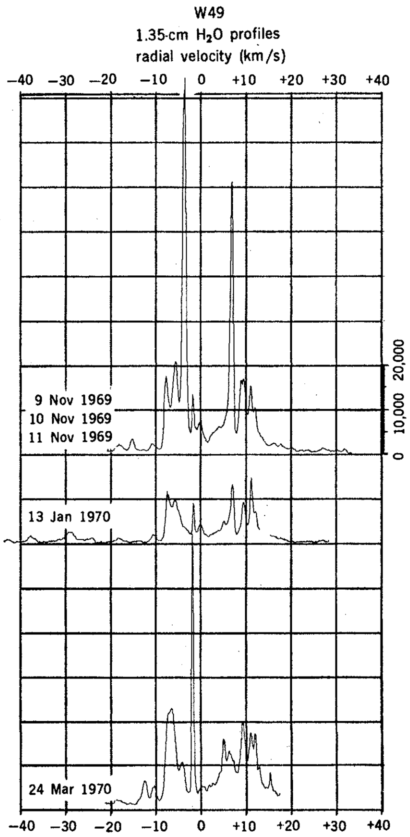

Fig. 10. Variations with time in the spectrum of masing clouds of H_2O in the radio source W49 [from W. T. Sullivan III (*48*)]. The highest peaks represent antenna temperatures of a few thousand degrees in an 85-foot antenna.

rected systems is then just as embarrassingly large as if each one is assumed isotropic.

Source sizes measured by interferometry are often as small as 10^{-8} radian, or in linear dimensions comparable with the earth's orbit (10^{13} cm). However, it is sometimes proposed that the amplifying medium is in fact much larger than the apparent source size, because radiation initiated from some localized region and at relatively low intensity can be amplified coherently and without distortion of its waveform as it progresses through a very extensive amplifying cloud. This proposal assumes that radiation from a small source is amplified as it travels through a cloud a few light years ($\sim 10^{18}$ cm) in extent. Such a possibility cannot be completely ruled out; however it seems clear that the more intense masers cannot involve amplification in large clouds. For H_2O, the states involved in maser action are about 450 cm^{-1} above the ground rotational state and decay to lower states in about 1 second. Hence, the amplifying medium must be at a moderately high temperature and excitations must occur frequently—if excitation is produced by collisions, the amplifying medium would have to be as dense as about 10^9 cm^{-3}, and such a dense cloud could not be very extensive. Furthermore, it can be shown that a large cloud could not give the large gains required without the occurrence in the cloud of scattering and spontaneous emission sufficient to send a wave of radiation backward at various angles through the cloud for further amplification. Such feedback by scattering, and amplification of spontaneous emission, tends to make the entire surface radiate incoherently, much like a very hot blackbody. It seems likely that at least the more intense masers are of this type, with radiation traversing the amplifying medium in all directions, and hence with the apparent size comparable with the actual size of the medium (*49*). This also implies molecular densities in the range from 10^9 to 10^{13} cm^{-3}, which makes the mass of the entire maser, at least for the more intense cases, comparable with a stellar mass.

The radiation of most laboratory masers or lasers is not random (Gaussian) in intensity, as is thermal noise or thermal radiation. Typical masers either produce spiky pulses or have a more or less constant output rather than random fluctuations. However, systems of the type suggested above, with random scattering to provide feedback, are known to provide random intensities (*50*). Recent careful examination of intensity fluctuations in interstellar OH masers (*51*) shows them to be random, just as is thermal radiation.

Pumping mechanisms for OH and H_2O masers are still uncertain. Clearly they involve some combination of collisions or excitation by radiation, and reradiation. In any case, they represent heat engines that require a high temperature source and a low temperature sink in order to continuously produce radiation at a very high temperature. Furthermore, any cyclic pumping scheme so far imagined for OH or H_2O requires the absorption or release by the molecules of a far infrared quantum of wavelength (about 100 microns) for every microwave quantum produced. This many far infrared quanta cannot be radiated into or out of the rather small surface of the masing systems at any reasonable temperature. This leads to the conclusion that both the source and sink for the maser pump are in most cases within the object (*49*). Hence, a reasonable structure for such a maser seems to be a rather dense cloud or envelope of gas and dust, with dimensions comparable with those of a large star and temperatures in the range of a few hundred to a few thousand degrees.

Probes of Isotopic Abundances

Molecular spectra offer an excellent opportunity to examine the relative isotopic abundances of common elements in various parts of interstellar space. For example, the difference between the isotopic mass of $^{12}C^{16}O$ and that of $^{13}C^{16}O$ gives approximately a 5 percent difference in moments of inertia and hence in rotational frequencies—an amount that separates the spectra of the two isotopic species enough so that they are very easily distinguished, but usually not so much as to prevent the intensities of the ^{12}CO and ^{13}CO lines from being measured with the same apparatus. When a given cloud of gas is optically thin at the molecular resonance, a simple comparison of intensities, with minor corrections for frequency ratios according to Eq. 7, gives the isotopic abundance ratios quite directly. Only in rare and special cases should the excitation of the two isotopic species be substantially different. If the cloud is optically thick, an accurate determination of the isotopic abundance ratios is not usually practicable, but at least approximate and limiting values can be obtained.

It is known that the relative abundances of the C, O, and N isotopes in such objects as the sun, meteorites, and comets do not differ much from those found on earth. However, there is no general reason to expect isotopic ratios to be the same in interstellar clouds as they are on earth or within the solar system. Yet in many cases these ratios seem to be rather similar.

The first ratio of isotopic abundances in interstellar gases that was determined from molecular microwave spectra was the $^{16}O : {}^{18}O$ ratio obtained by Rogers and Barrett (*52*) from the OH resonances in Sagittarius A. They estimated the $^{16}O : {}^{18}O$ ratio to be within a factor of two of the terrestrial one, 490. Later measurements gave 390 (*53*) and 314 (*54*) in this source and 203 in Sagittarius B2 (*54*). While the measured ratio of 390 is probably accurate to about 30 percent, this and the other measurements are not precise enough to demonstrate any definite difference between interstellar and terrestrial ratios. A ratio of about 20 for $^{16}O : {}^{18}O$ was obtained from the rather abundant molecule CO in the direction of Sagittarius B2 (*38*), when it was assumed that the optical depth is small. However, the authors note that this assumption is almost certainly incorrect for the $C^{16}O$ species, so that 20 is simply a lower limit for the ratio.

Deuterium represents one case where the isotopic abundance does differ from that on earth, as might be expected from the sensitivity of ^2H production and destruction rates to conditions of nuclear energy production. A lower limit to the average abundance ratio $^1H : {}^2H$ in interstellar space has been set by a comparison of the hyperfine structure resonance of ^2H with the intensity of the corresponding 21-cm line of ^1H. The resulting lower limit is $^1H : {}^2H >$ 13,000 (*55*) as compared with the terrestrial ratio, 6700.

The ratio $^{12}C : {}^{13}C$ has been obtained from several molecules in a number of sources. Usually, these measurements entail considerable uncertainty because the optical depths of the clouds are unknown. The ratios obtained, with the assumption of small optical depth in each case, are listed in Table 4.

The $^{12}C : {}^{13}C$ ratio is particularly interesting because the well-known carbon-nitrogen-oxygen (CNO) cycle for H burning in stars would produce, in equilibrium, the high ratio 4 (*56*), while He burning would essentially eliminate ^{13}C and produce a ratio approaching infinity. Thus, the isotopic abundance may give a good measure of past nuclear processing. The $^{12}C : ^{13}C$ ratio in the stars Alpha Orionis and Alpha Boötis appears to be about 3.5 (*57*) and 6 (*58*), respectively. The terrestrial value, 89, seems to be an accidental one resulting from nonequilibrium conditions, or from mixing of C from various sources, and yet values obtained from interstellar materials are not clearly very different from terrestrial ones. The values for $^{12}C : ^{13}C$ given in Table 4 are interesting and suggestive, but as yet give little definite information because the higher ratios usually occur in clouds with an appreciable but somewhat uncertain amount of optical depth, and hence are lower limits only. Recent high angular resolution work (*59*) on Sagittarius A indicates that correction for the optical depth gives a ratio of about 25 in that source. However, this value is valid only if the cloud density is rather uniform on the scale of the angular resolution obtained (~1 arc minute). The CH^+ measurement, from optical spectra in the direction of Zeta Ophiuchi, gives perhaps the best upper limit to the ratio because the resonances involved are not optically thick. The ratio obtained from the ultraviolet spectrum of CO in the same direction (*19*) also gives a good upper limit. Both values are quite close to the terrestrial one; perhaps this similarity occurs only because they represent measurements over part of our galaxy that is rather close (500 light years) to the earth, but perhaps the terrestrial value has some generality.

It is clear that more microwave measurements are needed of molecular resonances for cases where the optical depth of a cloud can be reliably established, or particularly where it is optically thin. Such measurements should be very valuable for understanding the origin of observed isotopic ratios and the history of interstellar materials.

Table 4. Intensity ratios of ^{12}C to ^{13}C from molecular spectra in a number of sources; these are the abundance ratios if it is assumed in each case that the source is optically thin. If this assumption is incorrect, as is probable in many of the cases listed, the measured result is a lower limit only. The terrestrial ratio is 89.

Molecule	Source	Intensity ratio ($\leq$ abundance ratio)	Reference
CH^+	Zeta Ophiuchi	82	(*13*)
CO	Zeta Ophiuchi	105	(*19*)
HCN	Orion	8.9	(*93*)
HCN	Sgr. A	4.7	(*93*)
H_2CO	Heiles' cloud 2	25	(*106*)
CO	Heiles' cloud 2	3	(*106*)
H_2CO	Sgr. A	11 ± 3	(*90*)
H_2CO	Sgr. B2	11 ± 2	(*90*)
H_2CO	W51	55 ± 30	(*90*)
CO	Sgr. A and B2	2	(*38*)

Probes of the Radiation Field

The 2.7°K isotropic radiation (*60*), sometimes called the relict or "big bang" radiation, has a strong effect on molecular excitation, as indicated above by Eqs. 1 and 3. While its intensity is rather well known to wavelengths as short as about 3 mm, there is relatively little information about the spectral intensity toward still shorter wavelengths and considerable curiosity over how well it agrees with a blackbody curve on the high frequency side. A blackbody distribution would give more assurance that the radiation was in fact produced by the initial explosion of the universe; large deviations would discount such an origin. However, deviations from a blackbody distribution that are not too drastic might be interpretable in terms of details of the early history of the universe.

The best information now available about the intensity of the isotropic radiation at wavelengths shorter than 3 mm, other than reports of very anomalous and perhaps unconnected radiation below 1 mm (*61*), comes from measurements of molecular excitation. The relative abundances of CN molecules in the ground and first excited rotational states establish an intensity of radiation at 2.63 mm that agrees with that expected from a blackbody at 2.7°K (*9–11*). Similar measurements of the next higher rotational state of CN and of the second rotational states of CH and CH^+ set upper limits on their populations and give only upper limits to the isotropic radiation at 1.32, 0.559, and 0.359 mm. These upper limits are of some value but are substantially greater than what is expected from 2.7°K blackbody radiation (*62*).

It seems likely that further measurement of the excitation of the wide variety of molecules now becoming known will be of great help in establishing the character of the high frequency part of the isotropic radiation. Such determinations require again a fairly detailed understanding of excitation mechanisms and in particular of the competition between collisions and radiative transitions. A study of the $2_{12} \rightarrow 2_{11}$ transition of H_2CO at about 2 cm gives information, for example, on the isotropic radiation at about 2.1 mm, because the latter radiation is important in establishing the populations of these levels relative to those of the 1_{10} and 1_{11} levels, between which the 6-cm H_2CO resonance occurs. So far, uncertainties in optical depths of clouds allow only an upper limit for isotropic radiation in the 2-mm region to be set from H_2CO observations. This upper limit is approximately seven times the intensity expected from 2.7°K blackbody radiation (*63*) and corresponds to a temperature of 5°K.

Formation and Disappearance of Molecules

The discovery of complex molecules in abundance came as something of a surprise to scientists, which indicates clearly that no obviously satisfactory mechanism for producing and maintaining them in interstellar space had been recognized prior to this. There are still no completely satisfactory mechanisms, though many possibilities have been discussed. The primary suggestions are:

1) Building up of molecules by binary collisions in the gaseous medium of interstellar space.

2) Formation of molecules on surfaces of dust grains from atoms or simpler molecules impinging on the surfaces.

3) Formation of molecules in the dense atmospheres of stars, perhaps largely by many-body collisions, and their subsequent expulsion into the interstellar medium.

4) Evaporation or decomposition of dust grains by bombardment, shock waves, or other heating processes. This suggestion reduces to the older problem of explaining the origin of dust grains; perhaps these originate in stellar atmospheres.

Any explanation of molecular formation must produce molecules as fast as they disappear, or accept a finite and sometimes short lifetime for the cloud of molecules. Hence, molecular disappearance is as important as molecular formation. One way in which molecules are eliminated is through dissociation by ionizing radiation; in clouds that are not very dense, ultraviolet light from stars is probably the most effective dissociation agent. Figure 11 indicates the dissociation energies of various molecular bonds and hence the energies of the ultraviolet photons required for their rupture. These are not always the lowest energies required for molecular dissociation, which corresponds, of course, to rupture of the weakest bond. The precise rate of molecular dissociation depends on details of the ultraviolet spectral distribution and the dissociation cross section. A recent evaluation of particular cases shows that such molecules as H_2O, NH_3, CH_4, and H_2CO dissociate in somewhat less than 100 years (*21, 64*) if exposed, unshielded by dust, to the average interstellar field of ultraviolet radiation. The molecule CO, with a considerably higher dissociation energy, has a lifetime of about 1000 years in the same field. One can judge from Fig. 11 that most other molecules would also dissociate within about 100 years with the exception of N_2, which can be expected to be longer-lived because of its strong bonding and to have a lifetime approximating that of CO. All of these lifetimes are so short that the molecules must either re-form rapidly or be very well shielded from ultraviolet radiation in order to have appreciable abundance in interstellar space. In the center of a dense cloud, of density 10^3 hydrogen molecules per cubic centimeter, 1 light year in extent, shielding of ultraviolet light by dust can be expected to reduce its intensity by about a factor of 10^{24}. Thus, much of the interior of such a cloud is almost free of ultraviolet starlight, and the more penetrating x-rays and cosmic rays may be dominating sources of molecular destruction, although the denser clouds even screen these out.

A second probably important mechanism for removing molecules from gas clouds is simply their freezing out—striking and adhering through van der Waals or other forces to the surfaces of dust grains. At the low temperatures of a few tens of degrees that seem characteristic of most dense clouds, the accommodation coefficient, that is, the probability of sticking to a surface on collision, is not very different from unity. The usual assumption that dust grains are of about 0.2-micron diameter and comprise about 1 percent of the mass of a cloud leads to the conclusion that the molecular lifetime before striking a dust grain is

$$\tau_g \approx \frac{10^{21}}{vn} \text{ seconds} \qquad (11)$$

where v is the molecular velocity and n the total molecular (hydrogen) density. Thus, for the denser clouds, with $n \approx 10^4$ cm^{-3} and $v \approx 3 \times 10^4$ cm/sec, $\tau_g \approx 3 \times 10^{12}$ seconds $= 10^5$ years. This freezing out is slower than ultraviolet dissociation of an unshielded molecule, but it takes place even for shielded molecules and gives them a free period in gaseous form that is probably substantially shorter than the lifetime of the cloud. Thus, regardless of the origin of the molecules, they must be regenerated or reemitted from the dust grain surfaces many times during the life of the cloud.

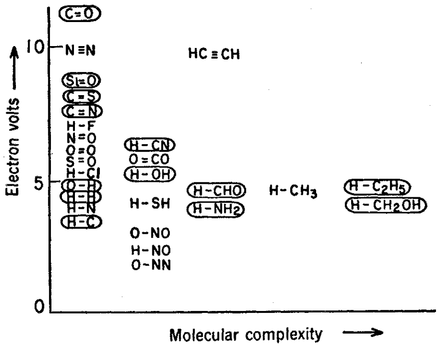

Fig. 11. Dissociation energies of various molecular bonds. In each case the bond referred to and its multiplicity are indicated. The molecules enclosed in capsules are those which have already been detected in interstellar space.

Binary collisions in the gas phase can in principle build up molecules, but the probability for a molecular combination forming from two colliding atoms appears too small in most cases to account for observed molecular abundances, particularly those of certain species for which the energy levels of the components and of the molecular combination are unfavorable. Binary ionic collisions, for example between H^- and H to form H_2 and an electron, are often more favorable than neutral collisions (*65*) and may in some cases be involved in the formation of H_2 (*66*). Julienne *et al.* (*67*) calculate that OH in the abundance observed may be formed by binary collision and an inverse predissociation process. Klemperer (*68*) has found that the observed abundances of CH, CH^+, and CN in the region between the earth and Zeta Ophiuchi can reasonably be explained by bimolecular collisions in a gas of density about 50 cm^{-3}. His calculation gives CO an abundance an order of magnitude greater than the abundances of these molecules; recent experimental results (*19*) show a CO abundance still greater by another order of magnitude. This calculation also indicates that NH and OH should be very uncommon, which means that formation of the molecules NH_3 and H_2O by such collisional processes is improbable.

The formation of molecules and dust grains in stellar atmospheres, which are much denser than interstellar clouds and allow many-body collisions, is well established (*69*). Furthermore, the total amount of material blown outward from stars and into interstellar regions can be shown to be not much less than the total material found in these regions (*70*). It is hence tempting to believe that both dust and molecules originate in stellar atmospheres or stellar eruptions. Such an origin seems likely for dust nuclei, which can of course contain molecules. However, the relatively short lifetimes of gaseous molecules in interstellar space makes their origin in stellar gaseous atmospheres questionable. It does not seem easy to sufficiently shield the molecules from stellar radiation so that they are not dissociated before getting well outside the radiation field of the star that forms them. Furthermore, once outside the radiation field of the star, molecules freeze out fairly rapidly on the cool dust grains, so that there must be mechanisms that regenerate the molecules or drive them off the grains during the life of the dust cloud. The latter process implies that molecules can equally well be formed on the surface of the dust grains and subsequently released into the gas phase.

Theoretical examinations of the formation of molecules in stellar atmospheres give interesting patterns for the relative abundances of various species (*69, 71*). For example, a star having more carbon than oxygen will combine oxygen mostly in the form of CO and the remainder of the carbon mostly in the form of CN and various hydrocarbons. If oxygen is more abundant than carbon, then most of the carbon is in the form of CO, and in addition H_2O is formed in some abundance. Thus, a stellar origin is consistent with abundant CO and could produce clouds of two distinct compositions, if it is assumed that a particular cloud comes primarily from a carbon-rich or from an oxygen-rich star. Calculations for neither of these types of stellar atmospheres predict any appreciable abundance of NH_3. The formation of this molecule by such a mechanism would appear to require stars with a large excess of nitrogen, a condition that nuclear reactions seem to allow (*56*) but that is uncommon.

Interstellar grains, which are undoubtedly far from perfect crystals, should provide many surface irregularities and active sites where an atom can be trapped until another reactive atom approaches and reacts chemically with it. The formation of complex molecules on surfaces in this fashion seems very likely (*72*); the mechanism for their release from the surface after formation is not so clear. The energy of the chemical reaction that forms the molecule is itself adequately large and may be effective in releasing the newly formed molecule from the surface. Alternatively, perhaps the impingement of a photon or an energetic particle on the surface can release the molecule. Perhaps still some other source of heat, such as a cosmic ray, can be effective in evaporating material from the grains.

Complex molecules similar to those observed in interstellar space have been shown to be produced by ultraviolet illumination of simple gases, such as H_2O, CO, and CO_2, adsorbed on dust grains (*73*). The production of molecules and their ejection from a tungsten surface by ultraviolet radiation has also been demonstrated (*74*). Thus, the formation of many varieties of molecules on dust grains in interstellar space presents no mystery, though the probability of their ejection from the surfaces of dust grains is not quantitatively known. Furthermore, how molecules that are condensed on dust grains are evaporated from them into the gaseous state is not clear. This leads to the last suggestion listed above.

Dust grains may be supplied with energy for the release of molecules not only by individual events, such as formation of a chemical bond or impingement of a photon or a particle, but also by more macroscopic heating processes. Perhaps the simplest example is the heating up of a dust cloud by a nearby hot star, possibly a new star formed from the cloud itself. Such heating would evaporate material condensed on dust grains, somewhat as molecules and radicals are evaporated from comets near the sun. Complex molecules on the dust grains could also be disintegrated into smaller units. In fact, OH and H_2O are particularly evident, through maser action, near regions where there is the release of considerable energy (*75*). Other suggested heating mechanisms that could disintegrate grains and produce molecules are shock waves due to gravitational instabilities within a dust cloud and collisions between two fast-moving clouds. The resulting high relative velocities between molecules and grains produce sputtering of the grain surfaces (*76*). In addition, direct collisions between dust grains at such velocities can provide sufficient energy for substantial evaporation (*77*).

Conclusions and Future Prospects

Recent discoveries of the microwave spectra of a considerable number of molecules prove the existence of rather complex molecules in interstellar clouds and provide probes for examining dense clouds, which are otherwise obscured by the dust they contain. In these clouds most of the gaseous material appears to be in the form of simple, relatively stable molecules, with atoms and free radicals much less abundant. While the abundances of molecular species generally decrease as their complexity increases, there are striking additional variations in the relative abundances of various species, and molecules with as many as seven atoms have already been found. New molecules are being discovered at a rapid rate; continued vigorous search and more sensitive receiving equipment can be expected to reveal many more, possibly doubling within 1 or 2 years the present total of almost 20 molecular types. The processes that form these molecules are not well understood, but they are probably dependent on dust grains associated with the gaseous clouds. Some molecular species have been found only in specific directions in certain very dense clouds. One such cloud is in the direction of the Orion nebula and another in Sagittarius B2, near the center of the galaxy. Others, such as CO and H_2CO, appear to be much more ubiquitous and are found in many more directions, and over large areas in particular clouds. Observation of such a variety of complex molecules is quite different from what has so far been seen in stellar atmospheres, or by other astronomical techniques. It provides information and insight into the character of dust clouds that has not previously been available.

While a wide range of temperatures, velocities, and densities have been indicated for dust clouds by the molecular observations, in general their temperatures appear low, in the range of tens of degrees Kelvin, and their densities are often strikingly high, from 10^3 to 10^6 hydrogen molecules per cubic centimeter. The clouds are frequently quite inhomogeneous and show rather large velocity spreads and temperature variations, and probably the denser ones are subject to considerable instability and activity, including the formation of stars.

The excitation of various molecular states is frequently far from thermodynamic equilibrium, as it is the result of competing collisional and radiation processes, some of which can be surmised from the observations. In at least one case this results in cooling the excitation temperature for two molecular levels considerably below the expected kinetic, dust, or radiation temperatures; in other cases the excitation is so great that the relative population in the upper and lower states is inverted, and maser-type amplification results.

Maser amplification and radiation, which is clearly observed from both OH and H_2O, is very intense and localized, the radiation coming from regions not much larger than the size of a large star and perhaps being associated with stellar processes.

Molecular spectra bear on a wide variety of astronomical problems. Some information that has already been obtained from molecular spectra on the relative abundances of H, C, O, and N isotopes should give clues to the origin and nuclear history of interstellar material. While there is an indication that the $^{12}C:^{13}C$ ratio is often surprisingly similar to that on Earth, uncertainties in optical densities and inhomogeneities in the clouds observed so far prevent any very certain conclusions. Molecular spectra promise also to yield valuable information on the universal isotropic microwave radiation through its effect on molecular excitation. The spectrum of OH from an external galaxy has recently been reported; this initiates the use of molecular spectra as probes of conditions in galaxies other than our own.

Both infrared and microwave radiation can penetrate the dense dust clouds where most molecules are found, and molecular spectra are abundant in both spectral regions. Infrared wavelengths easily allow, furthermore, much higher directivity than do microwaves, even in the largest radio telescopes. Hence, it is reasonable to hope that the development of infrared systems with very high spectral resolution and high sensitivity will provide additional powerful tools for exploring molecules and dust clouds. Much of this work can be carried out by ground-based observatories through the various infrared "windows" in the earth's atmosphere. However, important results can also be expected from observations from high-flying planes, balloons, or eventually satellites, for those regions of the infrared where the atmosphere absorbs strongly.

The recent observations add new importance to good microwave instruments, particularly receivers of high sensitivity and large antennas of sufficient surface accuracy for the millimeter region, which is particularly rich in molecular phenomena. With time, apparatus improvement in both these directions and marked enhancement of observations of molecular transitions can be expected.

As the number of observed molecular resonances grows, and as increased attention is directed toward intensive and systematic studies of their occurrence and characteristics, they should yield increasingly clear and detailed answers to many of the questions now investigated in only a preliminary way and point to additional useful investigations.

Molecular spectroscopy can be expected to be a major astronomical tool, in that it is now a rich and varied field and complements the more usual atomic spectroscopy, which has yielded much of our present understanding of astronomy. Molecular levels are typically much more closely spaced than are atomic levels and thus are convenient for the study of cool regions, rather than the higher temperature ones that are typically studied through atomic spectra. This, plus the penetrating properties of the longer wavelengths that are characteristic of molecular resonances, allows exploration of the extensive and important regions of dust clouds and probably the early states of stellar formation within them, and of the cooler components of external galaxies.

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DDT in the Biosphere: Where Does It Go?

Global modeling permits an appraisal of the hazards of DDT residues in the biosphere.

George M. Woodwell, Paul P. Craig, and Horton A. Johnson

DDT has been used in large quantities as an insecticide since 1942. Its residues (*1*) are sufficiently persistent and mobile to have a worldwide distribution, appearing in the lipids of most organisms (*2–7*), in air (*7–9*), and occasionally in meltwaters of Antarctic snows (*10*). Concentrations in certain of the earth's biota have reached toxic levels, causing spectacular declines in populations of certain carnivorous and scavenging birds and fish, aggravating the problems of pollution, and threatening significant contamination of human food chains (*2, 4, 11–14*). Recognition of the seriousness of these problems has led to recent restrictions in the use of DDT in the United States and abroad. There is at least a possibility that most of the DDT that has been or will ever be produced has already been used and that little, if any, will be applied after the mid-1970's (*15*). The persistence of DDT residues is great enough, however, that the residues will continue to be redistributed for many years after use of the pesticide has stopped, presumably presenting a continuing hazard to all the biota. The extensive data available on the distribution and effects of DDT make it, together with radioactive substances, the best known of the biospheric pollutants and a valuable subject for a case history study (*12, 16, 17*). But basic questions remain, among them the following: What becomes of DDT released into the biosphere? How serious are the hazards? and, How long will the hazards persist?

In an effort to answer these questions we have attempted to develop a model of the circulation of DDT in the biosphere. We have done this on the basis of two limiting assumptions: (i) that use of DDT will decline to zero by 1974 and, alternatively, (ii) that, between now and then, use will increase throughout the world.

Certain physical properties of DDT are important in determining its behavior in the biosphere. First, because of the high solubility of DDT in fats together with its low solubility in water (*18, 19*), DDT residues tend to accumulate in lipids and therefore in plants and animals. Second, the residues are very persistent in nature: estimates of their half-life range upward to 20 years, perhaps longer under certain circumstances (*20–24*). Third, DDT has a vapor pressure high enough to assure direct losses from plants and soil into the atmosphere, which can carry residues worldwide (*12, 13*). Thus soils, air, the waters of the oceans, and the biota are all potential reservoirs for DDT residues, and the hazard to the biota, including man, hinges on the distribution of DDT residues among these reservoirs. How large are the reservoirs, and what are the rates of exchange between them?

The answers are not available in any simple or absolute sense. Most are available, however, at least by inference. First, we must know how much DDT has been produced and something about its distribution.

Input: DDT Production

The amount of DDT produced in the United States each year is reported by the U.S. Tariff Commission (*25*). In the crop year 1963 the amount of DDT produced reached a maximum 8.13×10^{10} grams (179×10^6 pounds) (Fig. 1). Production has dropped in the United States since 1963, but more than 6.0×10^{10} grams of DDT were produced in 1969. Preliminary figures for 1970 reveal that DDT production declined by more than 50 percent. About 70 percent of the amount of DDT produced appears to have been used outside the United States. The total

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