

Interstellar Molecules: Chemicals in the Sky

The astronomers who participated in the special 1-day discussion on interstellar molecules during the 14th annual assembly of the International Astronomical Union (IAU) often joked that their research is becoming more and more like organic chemistry. Since the discovery in 1963 of interstellar microwaves from the hydroxyl radical (OH), no less than seven distinct molecules and two distinct radicals have been detected in the space between the stars. But the astronomers are hard-pressed for theoretical explanations of their observations of even the simplest of the interstellar molecules. Nonetheless, measurements of the properties of these interstellar molecules may provide valuable information about the evolution of stars and galaxies.

Most of the molecules were discovered with radio telescopes operating in the microwave region of the electromagnetic spectrum. Of course, studies in the optical region provided incentive for this work, and infrared and ultraviolet astronomy also make valuable contributions. One of the most exciting discoveries about the interstellar medium was recorded this year on an ultraviolet spectrum of the star Xi Persei taken during a rocket flight. Some of the absorption lines in the spectrum obtained by George Carruthers of the Naval Research Laboratory indicated that hydrogen molecules (H_2) are present in the medium between Xi Persei and the earth. The amazing finding is that the molecular hydrogen, which cannot be detected at radio wavelengths, has a density comparable to that of atomic hydrogen in the same direction. Since molecular hydrogen is believed to play a crucial role in the formation of stars, Carruthers' discovery may have profound effects on astrophysical theories.

The remaining molecules in space have been studied primarily by radio astronomers. They have successfully detected NH_3 (ammonia), H_2O , CO, H_2CO (formaldehyde), HCN (hydrogen cyanide), CN (cyanogen), and HC_3N (cyanoacetylene). Cyanoacetylene, the first five-atom molecule, was only discovered last June by B. E. Turner, of the National Radio Astronomical Observatory (NRAO), in the radiation from the galactic center. In this rapidly expanding field new molecules are continually being identified. At the IAU

meeting L. E. Snyder reported an unidentified line which he detected with D. Buhl, using the NRAO's 36-foot (12-m) telescope at Kitt Peak, Arizona. While they were investigating the signals from HCN in the lower side band of the receiver, the new line appeared in the upper side band. Snyder feels that it is a molecular line, but since it does not conform to any known molecule, he and his colleagues have dubbed it X-ogen. Snyder's group has detected X-ogen in several of the sources that also contain HCN (they first observed HCN in June). The unidentified line has a rest frequency of 89.190 ± 0.002 Ghz and has been seen in the sources Orion A, Sagittarius A, W3, and W51, and probably in source L134.

Although it is clear that these molecules exist in space and that they can emit radiation, there is no clear explanation of how they are formed and why they remain stable. Their chemical bonds should be broken by the intense fluxes of ultraviolet radiation and cosmic rays. Their estimated lifetimes from ultraviolet dissociation in interstellar space is about 200 years. However, the molecules which form in dark dust clouds are protected from this harsh environment. These clouds, which exist throughout the galaxy, help to stabilize their constituent molecules. The ultraviolet is absorbed in the outer regions of the dust clouds preventing it from breaking up molecules deep in the clouds' interior. It also is believed that the dust and ice in the clouds catalyze the formation of the molecules.

In spite of these basic difficulties, the interstellar molecules can be used to map the galactic distributions of certain elements and their isotopes, and to determine the temperature and velocity of the dust clouds. Measurements of the Doppler shift of the spectral lines give information about the velocity of the interstellar material. From these studies a complicated picture of the dynamics of the interstellar medium is beginning to emerge. For example, data from formaldehyde in the direction of the galactic center indicate that there may be a series of rotating concentric rings with the inner zones contracting and the outer ones expanding. Earlier work on the radio emissions from neutral atomic hydrogen allowed astronomers to map the spiral structures of our galaxy.

The isotopic abundances of the atomic elements present in the interstellar molecules can be determined by measuring the relative intensities of the lines corresponding to each isotope. Last year B. Zuckerman, P. Palmer, Snyder, and Buhl used interstellar formaldehyde to find the relative abundance of carbon-12 and carbon-13. They previously detected "normal" formaldehyde ($H_2^{12}C^{16}O$) by its absorption at 4830 Mhz. From measuring the equivalent absorption of its counterpart, $H_2^{13}C^{16}O$, which occurs at 4593 Mhz, the four radio astronomers arrived at a relative intensity for the two carbon isotopes which does not conform to any established theories. Their results for the $^{12}C/^{13}C$ abundance ratio is close to the value of 89 found on the earth and is much higher than the ratio found in stars. The stellar process currently favored by theorists gives a value less than 4 for $^{12}C/^{13}C$. The above-mentioned work on formaldehyde indicates the necessity of considerable rethinking on the question of how carbon is formed in our galaxy.

However, measurements of the carbon ratio in other molecules differ considerably from that of formaldehyde. Snyder and Buhl found a value of about 3.5 for the carbon ratio from the lines in HCN. Working at NRAO (Green Bank, West Virginia), Arno Penzias, Robert Wilson, and Keith Jefferts of Bell Telephone Laboratories have detected emission from both ^{12}CO and ^{13}CO . They find a ratio of about 2 for the carbon isotopes. At the IAU meeting both Snyder and Wilson mentioned that the carbon-12 lines from HCN and CO, respectively, must be heavily saturated to account for the formaldehyde ratio. Measurements on formaldehyde have also provided ratios for the oxygen isotopes ^{16}O and ^{18}O . Their relative abundance in space appears to be similar to the terrestrial value. As in the case of carbon, no satisfactory explanation for this ratio is yet available.

It is not clear when the study of interstellar molecules first began. In the 1920's optical astronomers detected diffuse features, rather than a discrete line, in absorption spectra from the interstellar medium. The current thoughts are that the diffuse line originates from molecules, but no definite identifications have been made.

At the IAU meeting two molecules were suggested as possible sources— $C_{46}H_{30}MgN_6$ [bis(pyridyl magnesium)tetrabenzoporphine] and SiC. During his talk on optical spectra, Dr. G. Herzberg of Ottawa drew attention to other candidates. From the results of laboratory studies, Herzberg proposed HCO , NH_4 , H_2O , CH_5 , and CH_4^+ as the sources of the diffuse spectra. Since these interstellar features remain unidentified, some astronomers prefer to date the first positive detection of molecules in space in the late 1930's when W. S. Adams observed lines in his optical spectra which belong to CN , CH^+ , and CH .

The first molecular structure discovered with radio telescopes has proved to be one of the most interesting. The absorption spectrum of OH was detected in 1963 by S. Weinreb, A. H. Barrett, M. L. Meeks, and J. C. Henry when they pointed the 84-foot aerial of the M.I.T. Lincoln Laboratory at the strong radio source Cassiopeia A. The well-known Russian astronomer I. S. Shklovsky had suggested that microwave emissions might also be detected. Armed only with the Russian's suggestion and with the OH microwave frequencies which were first measured by G. Ehrenstein, C. H. Townes, and M. J. Stevenson at Columbia University in 1959, the M.I.T. group gave radio astronomy a big boost. After the discovery of OH absorption, teams of researchers at several institutions began an intensive search for OH emission. When emission was found in 1965 by E. Gundermann and her associates at Harvard, and by H. Weaver and his associates at Berkeley, the properties of the signals were so peculiar that there was serious doubt whether the source was OH. Initially the observational facts could not be fit to preconceived notions concerning OH emission, and the Berkeley group believed that another molecule was also present. Since the other constituent could not be identified, it was given the name "mysterium."

When the results of other studies became available, it was clear that "mysterium" was not a necessary ingredient of the interstellar soup but that something unusual was occurring in the OH emission. The intensities of four known microwave lines in some of the OH spectra did not conform to the values expected from normal excitation processes. Radio astronomers also observed that in some cases the radiation was polarized, the features of the OH spectra fluctuated on the time scale of about

1 month, and the source of the emission occupied an exceedingly small volume in space. Since the sources are so small, they can only catch the astronomers' attention if they are extremely bright. Measurements of W3, for example, indicate a brightness temperature of 10^{13} °K. (This number is too large to have any physical significance.)

All of these anomalous characteristics led some astronomers to suggest that an exotic form of amplification, such as maser action, is occurring. To achieve maser-type amplification, populations of the energy levels that define the OH radio lines have to be inverted—that is, there must be more OH molecules in the higher energy level than in the lower energy level. When radio waves of the required frequency pass through such an inverted population, they stimulate transitions in the molecules so that all the new radiation constructively interferes. This correlation between the individual molecules amplifies the original signal. This type of amplifier, the maser, was discovered by Townes in the early 1950's, but it may have existed in the cosmos for millions of years. Masing not only explains the apparent brightness of the emission sources but it can also explain the fluctuations in the intensity. The gain sensitivity of man-made unsaturated masers is directly proportional to the inverted population of the atoms. Thus the intensity changes seem to signify that the natural OH masers would be unsaturated rather than saturated. However, since some features do not show fluctuations, they may be partially or totally saturated.

More recently it has been shown that interstellar H_2O exhibits properties that are similar to the OH sources. Water vapor was originally detected by the Berkeley group led by Townes. This group is also the discoverer of interstellar ammonia. It is interesting that the distribution of the OH emission in the galaxy is highly correlated with anomalous H_2O emission. Thus both of these masing molecular species may be influenced by the same phenomena.

In order to accurately measure the sizes and shapes of the masing regions, radio astronomers had to pool their resources. The resolution of a radio telescope is limited by the diffraction that occurs when the wave front of the radiation is truncated by a finite antenna. This problem has been partially solved through the use of radio interferometers. Two antennas separated from each other can give much higher resolution than could be obtained from

either one alone. When the signals from the two antennas are superimposed, the interference fringes provide a measure of the source's size. The first interferometer measurements of OH regions were taken with baselines of about 1 kilometer between the two detectors. Now an interferometer system, called the very long baseline interferometer (VLBI), which connects four stations separated by as much as 7720 kilometers is in operation. The four telescopes in the system are at Hat Creek, California; Green Bank, West Virginia; M.I.T.'s Lincoln Laboratory; and Onsala, Sweden. They have resolved one feature in W3 to about 0.0045 second of arc. In that W3 is believed to be about 5500 light-years away from the earth, this feature corresponds to a linear dimension about equal to the orbit of Mars! But until the actual emission process is known, these figures are only conjectures. Nonetheless, we can expect longer baselines to come into existence. There is even talk of placing one of the telescopes on the moon.

Despite all of the advances made in recent years, some large mysteries still remain. There is no explanation for the distribution of the molecules in space. Most of the dust clouds contain only a few molecular species. An even greater mystery is that some molecules that should be present have not been detected. In particular, searches for SiO , SO , H_2CS (thioformaldehyde), H_2C_2O (ketane), H_2CO_2 (formic acid), and NO have been unsuccessful. The mechanisms for the formation of the molecules are not understood. Work on the infrared at Kitt Peak and at the Minnesota observatories indicates that the molecules might originate in the atmospheres of red giant stars. Infrared photometry of these stars has revealed structure in their spectra attributable to silicate and graphite grains. Another suggestion is that the molecules are formed on interstellar grains.

In order to radiate, the molecules must first be excited to energy states above the ground state. Several processes have been proposed. These include collisions with neutral molecules such as hydrogen, and excitation by the isotropic background radiation that permeates the universe. However, considerable work is necessary before these proposals can be presented in all their details. Despite all of these unanswered questions, radio-astronomical observations of interstellar molecules have provided astrophysicists with solid data for their theories of stellar cosmogony.

—GERALD L. WICK